Anodic oxidation of catechols in the presence of α-oxoketene *N*,*N*-acetals with a tetrahydropyrimidine ring: selective α-arylation reaction†

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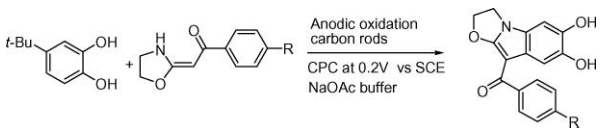
The electrochemical oxidation of catechols leads to the formation of *o*-benzoquinones. This property has been applied to effectively synthesize α-arylated products of α-oxoketene *N*,*N*-acetals with a tetrahydropyrimidine ring.

1. Introduction

Functionalized *o*-benzoquinones and their benzo-fused analogues have attracted a great deal of attention as a class of important intermediates for the synthesis of various biologically active products. Interest in the synthesis of these compounds leads to the development of numerous methods. Chemical oxidants, such as silver oxide,[1] potassium ferricyanide[2] or nonmetal organic catalysts[3] have been used to transfer catechols or 2-methoxyphenols to *o*-benzoquinones. Recently, periodate salt[4] or polymer supported periodate oxidant (ps-IO_4)[5] have also been used for the *in situ* generation of the *o*-benzoquinone intermediates. However, most of the conventional chemical oxidation approaches involve toxic oxidizing agents and/or metal additive, as well as stoichiometric oxidants, and are therefore regarded as non-environmentally benign processes.

Organic electrochemical synthesis in aqueous medium provides an alternative strategy for the synthesis and transformation of *o*-benzoquinones. Tabaković,[6] Nematollahi[7] and others[8] have studied the anodic oxidation of catechols in the presence of nucleophiles and observed that electrochemically-generated *o*-benzoquinones undergo Michael addition reaction to form various substituted catechols through an EC mechanism or benzofuran derivatives with diketo reagents through an ECEC mechanism. These electrochemical processes use electrons as oxidants and thus avoid the utilization of toxic metal-based reagents. From the viewpoint of green chemistry, it would be more attractive[9] to produce *o*-benzoquinones through an electrochemical method.

In order to discover polyhydroxylated aromatics as potential HIV-1 integrase inhibitors, we have also investigated the electrochemical oxidation of catechols in the presence of mercapto heterocycles and synthesized a variety of heterocyclic substituted catechols.[10] In view of the dinucleophilic property of enamines,[11] very recently, we have also explored the electrochemical oxidation of 4-*tert*-butylcatechol in the presence of α-oxoketene *N*,*O*-acetals[12] and developed a one pot electrochemical approach to the synthesis of fused indole derivatives containing active hydroxyl groups[13] (Scheme 1). This reaction may involve successive anodic oxidation, intermolecular Michael addition, anodic oxidation, enamine–imine tautomerization, imine–enamine tautomerization, intramolecular Michael addition and final aromatization process. In the present study, we further study the anodic oxidation of catechols in the presence of α-oxoketene acetals in which α-oxoketene *N*,*N*-acetals with a tetrahydropyrimidine ring have been used in place of α-oxoketene *N*,*O*-acetals. Results of this study indicate that α-aryl α-oxoketene *N*,*N*-acetals are obtained in moderate to good yields, instead of the corresponding fused indole derivatives. To the best of our knowledge, there is only one example involving the α-arylation reaction of α-oxoheterocyclic ketene *N*,*N*-acetals using 2,4-dinitrohalobenzenes as reactants by a radical nucleophilic substitution pathway.[14] Therefore, this protocol provides an efficient and complementary way to obtain α-aryl α-oxoketene *N*,*N*-acetals containing an electron-rich aromatic ring.



Scheme 1 A one-pot synthesis of fused indole derivatives from 4-*tert*-butylcatechol and α-oxoketene *N*,*O*-acetals with an oxazolidine ring.

2. Results and discussion

2.1 Electrochemical investigation of catechols in the absence and presence of α-oxoketene *N*,*N*-acetals by cyclic voltammetry

To conduct the electrochemical coupling reaction between catechols and α-oxoketene *N*,*N*-acetals with a tetrapyrimidine ring, the electrochemical properties of the starting materials need to be studied first. Taking 4-methylcatechol (**1b**) as an example, the electrochemical behavior of 2 mM catechols **1** in the absence and presence of α-oxoketene *N*,*N*-acetals **2** in 0.2 M acetate buffer at pH 7.0 were studied using cyclic voltammetry (CV) at a scan rate of 50 mV s^{-1} (Fig. 1). Due to the poor solubility of α-oxoketene *N*,*N*-acetals in water, acetonitrile was added as a co-solvent.

As shown in Fig. 1, in the absence of α-oxoketene *N*,*N*-acetal **2a**, the cyclic voltammogram of 4-methylcatechol consists of a well defined anodic peak (peak A_0) at +0.56 V, which is due to the two-electron oxidation of **1b** to its corresponding 4-methyl *o*-benzoquinone, and a corresponding cathodic peak (C_0) at +0.22 V

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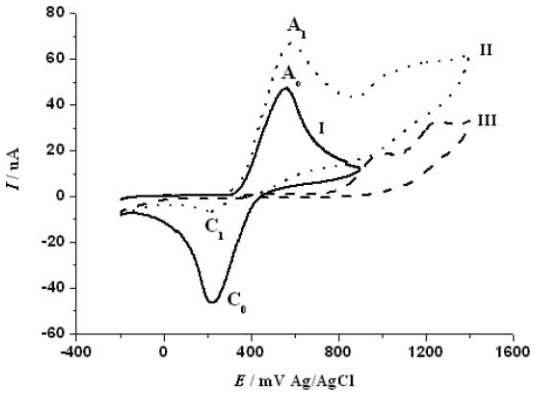


Fig. 1 Cyclic voltammograms of **1b** in the absence and presence of α-oxoketene *N*,*N*-acetal **2a**. I: 2 mM of **1b**; II: a mixture of 2 mM of **1b** and 2 mM of α-oxoketene *N*,*N*-acetal **2a**; III: 2 mM of α-oxoketene *N*,*N*-acetal **2a** at a glassy carbon working electrode, platinum wire counter, and Ag/AgCl (in 3 M KCl) reference electrode, in 1 : 1 (v/v) acetate buffer solution/acetonitrile (0.2 M, pH 7); scan rate 50 mV s^{-1}.

attributed to the reduction of 4-methyl *o*-benzoquinone back to 4-methylcatechol (curve I). The ratio of the current amplitudes between the oxidation and reduction processes is equal to unity (I_p^{ox}/I_p^{red}), indicating that the *o*-benzoquinone produced at the surface of the electrode is stable under pH 7 acetate buffer and that side-reactions such as hydroxylation or dimerization reactions are too slow to be observed on the time scale of the cyclic voltammetry.[7,8]

When one equivalent amount of α-oxoketene *N*,*N*-acetal **2a** was added, the height of the anodic peak A_1 for the oxidation of 4-methylcatechol increased, whereas that of the cathodic peak C_1 for the reduction of 4-methyl *o*-benzoquinone decreased (Fig. 1, curve II). Moreover, the anodic peak (A_1) of 4-methylcatechol in the presence of **2a** shifts slightly positive to 0.59 V compared to that in the absence of **2a**. Curve III in Fig. 1 is the CV of α-oxoketene *N*,*N*-acetal **2a**, where two irreversible anodic waves at 1.00 V and 1.25 V are observed. The observation that the anodic peak increased and cathodic peak decreased when **2a** was present indicates that the electrogenerated *o*-benzoquinone intermediate undergoes follow-up chemical reaction with **2a**.

The electrochemical behavior of other catechols in the absence and presence of α-oxoketene *N*,*N*-acetal **2a** were also investigated. The corresponding peak potentials were summarized in Table 1. As shown in Table 1, all of other catechols exhibit similar electrochemical pattern. For example, CV of **1a** itself gives a reversible anodic peak at 0.52 V and cathodic peak at 0.24 V, which move respectively to 0.54 V and 0.22 V in the presence of **2a**. Interestingly, no obvious changes of anodic and cathodic currents were observed when **2a** was added, which implied that the chemical reaction between electrogenerated 4-*tert*-butyl *o*-benzoquinone and **2a** occurred slowly.

Table 1 Peak potentials of catechols in the absence and presence of **2a**

	Peak potentials at GC[a,b]		Peak potentials at GC[a,c]		
Catechol	Ep_{ox}	Ep_{red}	Ep_{ox}	Ep_{red1}	Ep_{red2}
1a	0.52	0.24	0.54	0.22	—
1b	0.56	0.22	0.59	0.21	—
1c	0.52	0.30	0.57	0.29	—
1d	0.45	0.26	0.51	0.27	0.10

[a] Cyclic voltammetry measurements were performed in 0.2 M acetate buffer solution (pH 7); glassy carbon (GC) working electrode; scan rate 50 mV s^{-1}. Reference electrode: Ag/AgCl. [b] 2 mM of **1** in the absence of **2a**. [c] 2 mM of **1** in the presence of 2 mM of **2a**.

2.2 Electrochemical synthesis of compounds 3a–3n

On the basis of above CVs behavior of catechols in the absence and presence of α-oxoketene *N*,*N*-acetals, which is similar to that in the presence of α-oxoketene *N*,*O*-acetals, we can assume that a chemical step occurs between the electrochemically generated *o*-benzoquinones and the α-oxoketene *N*,*N*-acetals **2**, and then Michael addition products may be produced upon anodic oxidation of catechols and α-oxoketene *N*,*N*-acetals **2**. Thus, similar to our previous reaction conditions for a one-pot electrochemical synthesis of fused indole derivatives containing active hydroxyl groups,[13] the anodic oxidation of 4-*tert*-butylcatechol (**1a**) was performed in the presence of α-oxoketene *N*,*N*-acetal **2a** at controlled-potential at 0.3 V *versus* Ag wire[15] in acetate buffer using a divided cell. After 4-*tert*-butylcatechol was consumed, the formed precipitate was filtered, washed by water, dried and finally compound **3a** was isolated in 27% yield. However, the structure of **3a** was characterized to be a direct Michael addition and aromatization product, different from our previous results where indole derivatives were produced selectively from the anodic oxidation of the mixture of 4-*tert*-butyl catechol and α-oxoketene *N*,*O*-acetals with an oxazolidine ring. This observation indicates that the structure of α-oxoketene acetals (*N*,*O*-acetals or *N*,*N*-acetal) play a key role in the formation of either indoles or α-aryl α-oxoketene acetals.

Since electrochemical parameters, such as electrode materials, quantity of electric charge passed, solvents, supporting electrolytes, types of cell (divided cell or undivided cell) and mode of electrolysis (controlled potential or constant current), significantly affect the electrochemical results, 4-methylcatechol (**1b**) was then chosen as a model compound to investigate the appropriate conditions and then applied the optimized conditions to other catechols. Here, the mode of electrolysis (controlled potential or constant current) and types of cell (divided cell or undivided cell) were studied respectively (on the basis of our previous results, it is preferable to perform this type of reaction in buffer solution in the pH range of 6.0 to 8.0, using carbon rod as working electrode; therefore, other electrochemical parameters were not investigated). As shown in Table 2, the anodic oxidation of **1b** in the presence of **2a** was conducted at controlled-potential at 0.3 V *vs.* Ag wire[15] in a divided cell, affording **3b** in 52% yield. It decreased slightly to 50% when the same reaction was repeated in an undivided cell (beaker type cell). Next, the mode of electrolysis was investigated. As shown in Table 2, the yield of **3b** was 57% when the reaction was performed by using constant current technique in a divided cell, whereas it decreased to 43% in an undivided cell. This observation indicates that cell type seems to play a predominant role and the divided cell is preferable in the present coupling reaction.[16] In addition, controlled potential electrolysis gives a comparable yield *versus* that using constant current technique. One of the plausible reasons is a big difference in oxidizing potential between catechols and α-oxoketene

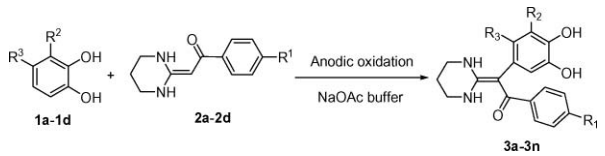
Table 2 Electrolysis of mixture of **1b** and **2a** under different conditions[a]

Entry	Current/mA	Electrolytic time/h	Electrolysis mode	Cell type	Yield of **3b**
1	15.9–17.4	1.6	Controlled potential[b]	Divided cell	52.0
2	15.0	1.5	Constant current	Divided cell	57.0
3	34.7–24.8	1.1	Controlled potential[b]	Undivided cell	50.0
4	15.0	1.5	Constant current	Undivided cell	43.0

[a] Acetate buffer: acetonitrile = 51.5 mL: 12.5 mL, 0.5 mmol **1b** and 0.5 mmol **2a**; passed charge: 2.24 F mol^{-1}; room temperature. [b] Controlled potential at 0.3 V *vs.* Ag wire.

N,*N*-acetals, which mean α-oxoketene *N*,*N*-acetals were not oxidized or were difficult to oxidize when the mixture of catechols and α-oxoketene *N*,*N*-acetals was electrolysized using either constant current or controlled-potential techniques.

Considering that a potentiostat is considerably more expensive and not always available in organic synthesis laboratory. Moreover, comparable yields can afford when using either constant current electrolysis or controlled-potential electrolysis mode. Therefore, constant current electrolysis in divided cell seems to be preferable and then is employed for the electrochemical oxidation of other catechols in the presence of α-oxoketene *N*,*N*-acetals with a tetrahydropyrimidine ring **2** (Scheme 2).



Scheme 2 Anodic oxidation of a mixture of catechols **1** and α-oxoketene *N*,*N*-acetals **2**.

Thus, anodic oxidation of 4-*tert*-butylcatechol (**1a**) in the presence of **2a** was repeated at a constant current of 15 mA (~3 mA cm^{-2}) in the divided cell. The corresponding product **3a** was achieved in 25%. (Table 3, entry 1). Similarly, compound **3c** was produced in 32% yield upon constant current electrolysis of the mixture of caffeic acid and **2a** in the phosphate buffer solution.[17] It is worth noting that, in this case, **3c** did not precipitate directly from the electrolytic mixture. Moreover, it was observed that compound **3c** decomposed when flash chromatography was used to isolate the reaction mixture. Then, the reaction solutions (water and acetonitrile) were first removed partially under reduced pressure and solid precipitated. The desired compound **3c** was finally obtained after filtering and recrystallizing from a mixed solution of methanol and water.

Subsequently, the reaction was applied to 3-substituted catechols such as 3-methoxycatechol (**1d**) with a view to investigate the scope of the reaction. In a similar way, electrochemical oxidation of **1d** in the presence of **2a** was performed and the expected products **3d** were accomplished in 54% yield (Table 3, entry 4).

In order to evaluate the versatility of the reaction further, a series of α-oxoketene *N*,*N*-acetals were also investigated by a similar procedure. As shown in Table 3, the electrochemical oxidations of 4-*tert*-butylcatechol (**1a**) in the presence of 1-phenyl-2-(tetrahydropyrimidin-2(1*H*)-ylidene)ethanone (**2b**), 1-(*p*-methylphenyl)-2-(tetrahydropyrimidin-2(1*H*)-ylidene)ethanone (**2c**), or 1-(*p*-methoxyphenyl)-2-(tetrahydropyrimidin-2(1*H*)-ylidene)-ethanone (**2d**) also proceeded smoothly, yielding the desired **3e**, **3f** and **3g** in 68%, 39% and 46% yields, respectively (Table 3, entries 5–7).

Similarly, when 4-methylcatechol was subjected to anodic oxidation in the presence of **2b**, **2c** or **2d** under same conditions, desired α-aryl α-oxoketene *N*,*N*-acetals **3h–3j** were afforded in 49%, 82% and 40% yields, respectively (Table 3, entries 8–10).

In addition, when caffeic acid was anodically oxidized in the presence of **2b**, **2c** or **2d**, the corresponding α-aryl α-oxoketene *N*,*N*-acetals **3k–3m** were afforded in reasonable yield. (Table 1, entries 11–13).

Finally, compound **3n** was produced in 59% yield from the constant current electrolysis of a mixture of **1d** and **2c** (Table 3, entry 14).

It is worth noting that compounds **3** appear not stable and could not survive from column chromatography isolation. The only way to purify is to make the products precipitate and then recrystallize. Therefore, the exact yields of compounds **3** should be higher than that reported in Table 3, which is based on the precipitated amounts.

On the basis of above results, we can conclude that the nature of dinucleophile plays a key role in the formation of products. When the dinucleophiles are α-oxoketene *N*,*O*-acetals, indole derivatives are produced. However, it affords exclusively α-arylation products when the dinucleophiles are *N*,*N*-acetals. Therefore, our present work provides an efficient method to obtain α-aryl α-oxoketene *N*,*N*-acetals containing electron-rich aromatic ring.

The structures of **3a–n** were characterized by using ^{1}H NMR, ^{13}C NMR, IR and ESI-MS. First of all, ESI-MS results strongly suggests that compounds **3** are the coupling products of α-oxoketene *N*,*N*-acetal moieties and catechol scaffolds. The structures of these compounds were then elucidated by NMR spectroscopy. The ^{1}H NMR spectra of products from the reaction of 4-substituted catechols and **2** displays two singlets of aromatic protons. The ^{1}H NMR spectrum of the compounds from the reaction of 3-substituted catechols and **2** exhibits two *meta*-oriented aromatic proton signals (doublets, $J = 2.0$ Hz). These results are consistent with the 1,4-addition products, which indicates that the α-carbon atom of α-oxoketene *N*,*N*-acetal moieties always attack selectively the carbon atom of the catechol scaffold that is the *para*-position (rather than the *ortho*-position) of one of the two OH groups of the benzene ring (Fig. 2).

2.3. Mechanism

On the basis of the above results and related work by others,[7,8] an EC mechanism can be speculated for the formation of compounds **3**. As described in Scheme 3, the initial step is an electrochemical process that involves the oxidation of catechols **1** on the anodic

Table 3 Electrochemical synthesis of α-aryl α-oxoketene *N*,*N*-acetals **3** containing the catechol subunit[a]

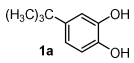
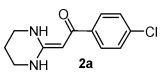
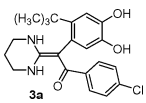
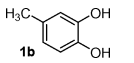
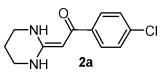
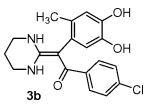
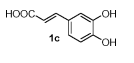
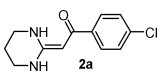
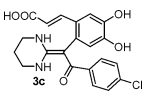
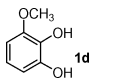
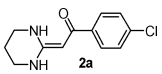
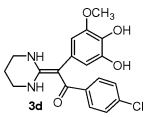
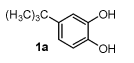
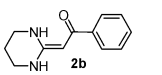
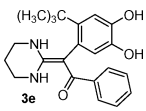
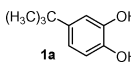
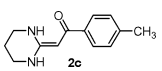
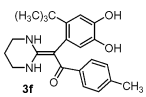
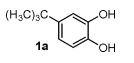
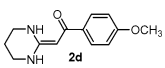
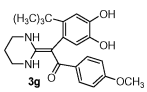
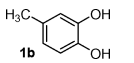
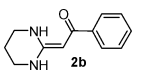
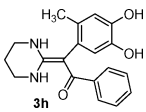
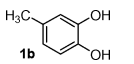
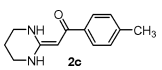
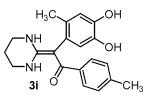
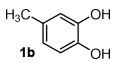
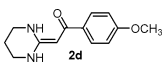
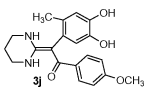
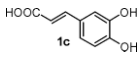
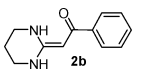
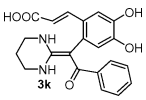
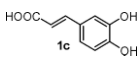
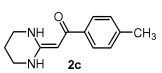
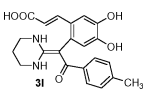
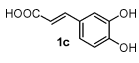
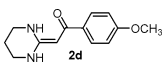
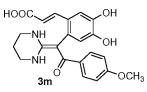
Entry	Catechol **1**	Ketene *N*,*N*-acetal **2**	Product	Yield
1				27[b,f] 25[b]
2				57[b] 79[b,e]
3				32[d]
4				54[b]
5				68[b]
6				39[b]
7				46[b]
8				49[b]
9				82[c]
10				40[d]
11				20[d]
12				76[d]
13				25[d]

Table 3 *(Contd.)*

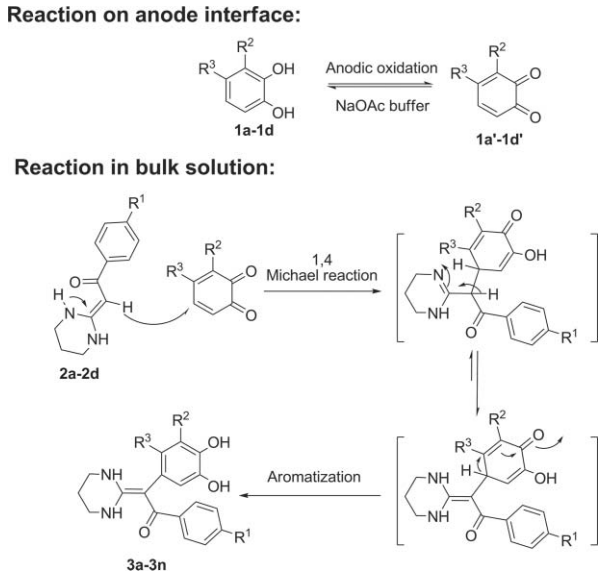
Entry	Catechol **1**	Ketene *N*,*N*-acetal **2**	Product	Yield
14				59[c]

[a] Reaction conditions: constant current at 15 mA (3 mA cm^{-1}), graphite rod anode, Pt wire cathode and divided cell. [b] The product precipitated from the electrolytic solution, which was filtered and washed by water to give a high quality product. [c] The products did not precipitate from the electrolytic solution. After removal of the mixed solution under reduced pressure, the residue was re-dissolved in methanol and acidified with hydrochloride to pH 1. The mixture was kept in refrigerator overnight. The formed solid (NaCl) was removed and the filtrate was recrystallized in a mixed solution of methanol and water. [d] Phosphate buffer was used as the electrolyte. In this case, the products did not precipitate from the electrolytic solution. After removal of partial solution under reduced pressure, the desired products precipitated and were obtained after filtering and recrystallizing from mixed solution of methanol and water. [e] The reaction was performed at 0 °C. [f] The reaction was performed under controlled-potential at 0.3 V *vs.* Ag wire in divided cell.

Fig. 2 Partial ^{1}H NMR spectra of compound **3b** and **3d** showing regioselective products from 1,4-addition.

electrode surface, generating the corresponding *o*-benzoquinones, which diffuses to the bulk electrolytic solution. Subsequently, a chemical reaction occurs between the active *o*-benzoquinone intermediates and the α-carbon atom of the α-oxoketene *N*,*N*-acetals **2** through a Michael addition reaction followed by an aromatization process leading to products **3**.

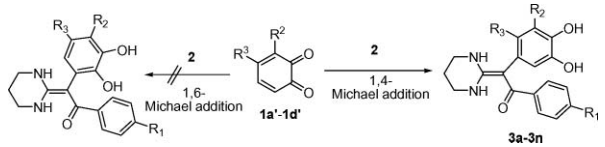
It is worth mentioning that the electrochemical oxidation of 4-*tert*-butylcatechol and 3-substituted catechols in the presence of α-oxoketene *N*,*O*-acetals (the analogues of *N*,*N*-acetals **2**) can achieve a one-pot electrochemical synthesis of fused indole derivatives in the range of 37–71% yields.[13] In addition, it was reported that the putative *o*-benzoquinone derivatives stemmed from the anodic oxidation of dopamine undergoes rapid intramolecular cyclization, leading to a redox active indoline derivative, which, after subsequent oxidation, rapidly affords insoluble melanin-like polymer.[18] In view of the facts that compounds of type **3** were also typical catechol derivatives, and therefore over-oxidation of compounds **3** followed by further intramolecular Michael addition



Scheme 3 A plausible mechanism between catechols **1** and ketene *N*,*N*-acetals **2** under the anodic oxidation conditions.

was expected to occur and cause the formation of corresponding indole derivatives. However, it is observed that α-arylated α-oxoketene *N*,*N*-acetals **3** were produced exclusively. The reason behind this is not clear, although the nature of the starting α-oxoketene *N*,*N*-acetals may play a predominant role.

In addition, principally, *o*-benzoquinone derivatives may undergo 1,4-addition and 1,6-addition with nucleophiles and therefore a couple of regioisomers may generate (Scheme 4). Moreover, it was reported that 1,6-addition products have been obtained as predominant products from reaction of various *o*-benzoquinones with SH-containing nucleophiles such as cysteine, *N*-acetylcysteine and glutathione at physiological pH, due to intramolecular base catalysis and greater softness of the sulfur atom.[8] However, in our cases, only 1,4-addition adducts were obtained. We have calculated the distribution of the coefficients of the LUMO of *o*-benzoquinone (see the ESI†), and the result shows that there is no obvious difference between C3 and C4 atoms. Therefore, the regioselective outcome may be rationalized in the terms of the greater hardness of the α-carbon atom of ketene *N*,*N*-acetals **2**, which prefers attacking the more electropositive C position of the quinone ring.



Scheme 4 Possible regioselective reaction of *o*-benzoquinones **1** and ketene *N*,*N*-acetals **2**.

3. Conclusion

In summary, anodic oxidation of catechols **1** in the presence of α-oxoketene *N*,*N*-acetals with a tetrahydropyrimidine ring **2** have been investigated by cyclic voltammetry and constant current electrolysis methods. The results indicate that the electrochemically generated *o*-benzoquinones undergo 1,4-Michael addition with α-oxoketene *N*,*N*-acetals **2** following an EC mechanism to afford exclusively α-aryl α-oxoketene *N*,*N*-acetals **3** in moderate to good yield, which provides an electrochemical oxidization approach for the arylation reaction of α-oxoketene *N*,*N*-acetals. Further studies towards the synthetic application (for example, further transformation to indoles) are current under way in our group.

4. Experimentals

4.1 Instruments and reagents

All melting points were measured with a XT4A Electrothermal melting point apparatus and are uncorrected. IR spectra were recorded as KBr pellets. ^{1}H and ^{13}C NMR spectra were recorded with an AV 400M Bruker spectrometer (400 MHz ^{1}H frequency, 100 MHz ^{13}C frequency). Chemical shifts are given as δ values (internal standard: TMS). The MS spectra (ESI) were recorded on a Bruker esquire 6000 mass spectrometer.

Catechols **1a–d** were reagent-grade from Alfa Aesar China (Tianjin) Co. Ltd. Compounds **2a–d** were synthesized according to the known procedure.[19] Other chemicals and solvents were from Beijing Chemicals Co. and used without further purification. All electrodes for CV experiments were from CH Instruments, Inc. USA. Doubly distilled de-ionized water was used for preparation of aqueous acetate buffer. All experiments were performed at room temperature and ambient pressure.

4.2 Cyclic voltammetry

Cyclic voltammograms were measured by a 273A Potentiostat/Galvanostat equipped with an electrochemical analysis software, using a conventional three-electrode cell. The working electrode was a glassy carbon disk electrode (*ca.* $\phi = 3$ mm). The auxiliary and reference electrodes in these studies were Pt wire and saturated Ag/AgCl (in 3 M KCl), respectively. Glassy carbon was polished with polishing cloth before each measurement. Acetate buffer solution was prepared by NaAc and HAc monitored by a digital pH meter. Scan rate was 50 mV s^{-1}. The concentration of **1** and **2** were 2 mmol L^{-1}, while that of the supporting electrolyte was 0.2 mol L^{-1}.

4.3 General procedure for the synthesis of compounds 3a–3n by constant current electrolysis

A 100 mL of H-type cell was equipped with a medium glass frit as a membrane. The anode compartment contained an assembly of 7 graphite rods as the anode, whose upper rims were wrapped by a copper wire, and a platinum wire as the counter electrode was immersed in the cathode compartment. The applied current throughout electrolysis was 15 mA and was controlled by a D.C. regulated power supply. During electrolysis, a magnetic stirrer stirred the mixture.

In a typical procedure, to the anode compartment which is kept in water at room temperature (in the range of 23–25 °C) was added a mixture of 52 mL acetate buffer solution (pH 6) (or phosphate buffer solution) and 12 mL of acetonitrile. Subsequently, 1 mmol catechols **1** and 1 mmol 1-(substituted)-phenyl-2-(tetrahydropyrimidin-2(1*H*)-ylidene)ethanone **2** were added to the anodic compartment and electrolyzed. The electrolysis was

terminated when the starting **1** was consumed by TLC following the reaction process. After electrolysis, the anolyte was worked up by one of the methods as indicated below to obtain desired compounds **3**.

The product precipitated from the electrolytic solution, then the reaction mixture was filtered and the solid was washed with water to give high quality of products.

The product did not precipitate from the electrolytic solution. Then, after removal of the anolyte under reduced pressure, the residue was re-dissolved in methanol and acidified with hydrochloride to pH 1. The mixture was maintained in refrigerator overnight. The formed solid (NaCl) was removed and the filtrate was recrystallized in methanol–water to afford products.

Phosphate buffer solution was used as electrolyte. In these cases, the product did not precipitate from the electrolytic solution. Then, after partial removal of the solution under reduced pressure, the desired products precipitated, which were purified using recrystallization from mixed solution of methanol and water.

4.3.1. 2-(2-*tert*-Butyl-4,5-dihydroxyphenyl)-1-(4-chlorophenyl)-2-(tetrahydropyrimidin-2(1*H*)-ylidene)ethanone (3a). Yield: 25%; mp: 225–226 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.04 (s, 9H, C(CH$_3$)$_3$), 1.72-1.82 (m, 2H, CH$_2$), 3.16 (s, br, 2H, CH$_2$), 3.33-3.37 (m, 2H, CH$_2$), 5.42 (s, br, 1H, NH), 6.40 (s, 1H, Ar–H), 6.76 (s, 1H, Ar–H), 7.07 (d, 2H, J = 8.4 Hz, Ar–H), 7.14 (d, J = 8.4 Hz, 2H, Ar–H), 8.66 (s, 2H, OH), 12.72 (s, br, 1H, NH); ^{13}C NMR (100 MHz, DMSO-d_6): δ 20.5, 32.5, 36.2, 38.1, 96.2, 116.8, 124.2, 124.9, 127.0, 130.6, 132.0, 141.6, 143.2, 143.3, 144.7, 160.1, 177.3; IR (KBr): ν 3413, 3001, 2958, 2874, 1603, 1584, 1522, 1504, 1483; ESI-MS: m/z 400.9 (M$^+$+1), 801.1 (2M$^+$+1), 398.8 (M$^-$−1), 799.0 (2M$^-$−1).

4.3.2. 1-(4-Chlorophenyl)-2-(4,5-dihydroxy-2-methylphenyl)-2-(tetrahydropyrimidin-2(1*H*)-ylidene)ethanone (3b). Yield: 57%; mp: 222–223 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.79 (s, 2H, CH$_2$), 1.86 (s, 3H, CH$_3$), 3.26-3.34 (m, 4H, CH$_2$), 5.56 (s, br, 1H, NH), 6.33 (s, 1H, Ar–H), 6.48 (s, 1H, Ar–H), 7.00 (d, 2H, J = 8.4 Hz, Ar–H), 7.08 (d, 2H, J = 8.4 Hz, Ar–H), 8.47 (s, 1H, OH), 8.58 (s, 1H, OH), 12.38 (s, br, 1H, NH); ^{13}C NMR (100 MHz, DMSO-d_6): δ 19.6, 20.4, 38.6, 92.7, 117.8, 121.8, 126.9, 127.2, 129.5, 130.0, 131.7, 143.4, 143.7, 144.6, 159.3, 179.9; IR (KBr): ν 3468, 3287, 2936, 2879, 1642, 1600, 1500, 1483; ESI-MS: m/z 358.7 (M$^+$+1), 716.7 (2M$^+$+1), 356.7 (M$^-$−1), 714.9 (2M$^-$−1).

4.3.3. (*E*)-3-{4,5-Dihydroxy-2-[2-oxo-2-(4-chlorophenyl)-1-(tetrahydropyrimidin-2(1*H*)-ylidene)]ethyl}phenylacrylic acid (3c). Yield: 32%; mp: 186–188 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.77 (t, J = 5.2 Hz, 2H, CH$_2$), 3.15-3.24 (m, 4H, CH$_2$), 5.75 (s, br, 1H, NH), 5.89 (d, J = 16.0 Hz, 1H, CH=CH), 6.40 (s, 1H, Ar–H), 6.89 (d, J = 8.8 Hz, 2H, ArH), 6.94 (s, 1H, Ar–H), 7.02 (d, J = 8.8 Hz, 2H, ArH), 7.44 (d, J = 16.0 Hz, 1H, CH=CH), 12.30 (s, br, 1H, NH); ^{13}C NMR (100 MHz, DMSO-d_6): δ 20.3, 90.9, 113.5, 115.3, 121.9, 127.2, 127.4, 129.4, 130.7, 131.7, 143.5, 145.3, 148.4, 159.3, 168.6, 180.9; IR (KBr): ν 3435, 1636, 1510; ESI-MS: m/z 414.9 (M$^+$+1), 828.2 (2M$^+$+1), 412.6 (M$^-$−1).

4.3.4. 1-(4-Chlorophenyl)-2-(3,4-dihydroxy-5-methoxyphenyl)-2-(tetrahydropyrimidin-2(1*H*)-ylidene)ethanone (3d). Yield: 54%; mp: 245 °C (dec); ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.80 (s, 2H, CH$_2$), 3.27-3.33 (m, 4H, CH$_2$), 3.56 (s, 3H, OCH$_3$), 6.05 (s, 1H, Ar–H), 6.07 (s, 1H, Ar–H), 7.05 (d, J = 8.0 Hz, 2H, ArH), 7.10 (d, J = 8.4 Hz, 2H, ArH), 8.03 (s, 1H, OH), 8.64 (s, 1H, OH), 12.28 (s, br, 1H, NH); ^{13}C NMR (100 MHz, DMSO-d_6): δ 25.0, 43.3, 60.9, 99.7, 114.6, 119.4, 131.9, 132.2, 134.6, 136.2, 137.9, 148.6, 150.7, 153.3, 164.2, 185.3; IR (KBr): ν 3417, 2975, 2942, 2870, 1607, 1574, 1464; ESI-MS: m/z 374.9 (M$^+$+1), 372.6 (M$^-$−1).

4.3.5. 2-(2-*tert*-Butyl-4,5-dihydroxyphenyl)-1-phenyl-2-(tetrahydropyrimidin-2(1*H*)-ylidene)ethanone (3e). Yield: 68%; mp: 243 °C (dec); ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.04 (s, 9H, C(CH$_3$)$_3$), 1.74-1.81 (m, 2H, CH$_2$), 3.16 (s, 2H, CH$_2$), 3.37 (s, 2H, CH$_2$), 5.32 (s, br, 1H, NH), 6.42 (s, 1H, Ar–H), 6.74 (s, 1H, Ar–H), 7.01-7.016 (m, 5H, Ar–H), 8.62 (s, 2H, OH), 12.81 (s, br, 1H, NH); ^{13}C NMR (100 MHz, DMSO-d_6): δ 20.6, 32.5, 36.2, 39.6, 96.1, 116.7, 118.5, 124.3, 125.3, 127.0, 127.3, 128.8, 141.6, 143.1, 144.5, 160.0, 179.1; IR (KBr): ν 3415, 2959, 2870, 1602, 1582, 1501, 1485; ESI-MS: m/z 366.9 (M$^+$+1), 733.1 (2M$^+$+1), 364.8 (M$^-$−1), 731.0 (2M$^-$−1).

4.3.6. 2-(2-*tert*-Butyl-4,5-dihydroxyphenyl)-2-(tetrahydropyrimidin-2(1*H*)-ylidene)-1-*p*-tolylethanone (3f). Yield: 39%; mp: 247–249 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.05 (s, 9H, C(CH$_3$)$_3$), 1.72-1.81 (m, 2H, CH$_2$), 2.16 (s, 3H, CH$_3$), 3.16 (s, 2H, CH$_2$), 3.33-3.37 (m, 2H, CH$_2$), 5.26 (s, br, 1H, NH), 6.39 (s, 1H, Ar–H), 6.75 (s, 1H, Ar–H), 6.82 (d, 2H, J = 8.0 Hz, Ar–H), 7.04 (d, J = 8.4 Hz, 2H, Ar–H), 8.61 (s, 2H, OH), 12.85 (s, br, 1H, NH); ^{13}C NMR (100 MHz, DMSO-d_6): δ 20.6, 21.1, 32.5, 36.2, 38.1, 95.8, 116.7, 124.3, 125.5, 127.6, 128.8, 136.5, 141.5, 141.7, 143.1, 144.5, 159.9, 179.0; IR (KBr): ν 3382, 2947, 1595, 1523, 1494, 1416; ESI-MS: m/z 380.8 (M$^+$+1), 761.1 (2M$^+$+1), 378.8 (M$^-$−1), 759.1 (2M$^-$−1).

4.3.7. 2-(2-*tert*-Butyl-4,5-dihydroxyphenyl)-1-(4-methoxyphenyl)-2-(tetrahydropyrimidin-2(1*H*)-ylidene)ethanone (3g). Yield: 46%; mp: 232–233 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.06 (s, 9H, C(CH$_3$)$_3$), 1.72-1.81 (m, 2H, CH$_2$), 3.16 (s, br, 2H, CH$_2$), 3.31-3.37 (m, 2H, CH$_2$), 3.65 (s, 3H, OCH$_3$), 5.21 (s, br, 1H, NH), 6.40 (s, 1H, Ar–H), 6.56 (d, 2H, J = 8.8 Hz, Ar–H), 6.79 (s, 1H, Ar–H), 7.12 (d, J = 8.8 Hz, 2H, Ar–H), 8.62 (s, 2H, OH), 12.91 (s, br, 1H, NH); ^{13}C NMR (100 MHz, DMSO-d_6): δ 20.7, 32.4, 36.2, 38.1, 55.3, 95.5, 112.2, 116.7, 124.2, 125.8, 130.4, 136.9, 141.6, 143.2, 144.5, 158.8, 159.9, 178.3; IR (KBr): ν 3416, 2965, 1600, 1511, 1490; ESI-MS: m/z 396.8 (M$^+$+1), 793.1 (2M$^+$+1), 394.8 (M$^-$−1), 791.0 (2M$^-$−1).

4.3.8. 2-(4,5-Dihydroxy-2-methylphenyl)-1-phenyl-2-(tetrahydropyrimidin-2(1*H*)-ylidene)ethanone (3h). Yield: 49%; mp: 247 °C (dec); ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.79-1.80 (m, 2H, CH$_2$), 1.88 (s, 3H, CH$_3$), 3.26-3.34 (m, 4H, CH$_2$), 5.50 (s, br, 1H, NH), 6.34 (s, 1H, Ar–H), 6.45 (s, 1H, Ar–H), 7.00-7.04 (m, 5H, Ar–H), 8.43 (s, br, 1H, OH), 8.50 (s, br, 1H, OH), 12.48 (s, br, 1H, NH); ^{13}C NMR (100 MHz, DMSO-d_6): δ 19.6, 20.5, 38.5, 92.61, 117.8, 121.9, 127.1, 127.3, 127.7, 130.0, 143.3, 144.4, 144.9, 159.3, 181.6; IR (KBr): ν 3393, 1595, 1524, 1500; ESI-MS: m/z 324.8 (M$^+$+1), 649.0 (2M$^+$+1), 322.6 (M$^-$−1), 646.8 (2M$^-$−1).

4.3.9. 2-(4,5-Dihydroxy-2-methylphenyl)-2-(tetrahydropyrimidin-2(1*H*)-ylidene)-1-*p*-tolylethanone (3i). Yield: 82%; mp: 208–209 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.85 (t, J = 5.6 Hz, 2H, CH$_2$), 2.23 (s, 3H, CH$_3$), 2.33 (s, 3H, CH$_3$), 3.31-3.38 (m, 4H, CH$_2$), 6.21 (s, 1H, NH), 6.27 (s, 1H, Ar–H), 6.73 (s, 1H,

Ar–H), 7.30 (d, 2H, $J = 8.0$ Hz, Ar–H), 7.72 (d, 2H, $J = 8.0$ Hz, Ar–H), 8.90 (s, 1H, OH), 9.23 (s, 1H, OH), 9.46 (s, 1H, NH); ^{13}C NMR (100 MHz, DMSO-d_6): δ 18.2, 19.1, 21.6, 53.9, 117.4, 119.2, 120.0, 128.0, 129.4, 129.9, 132.8, 143.9, 145.1, 146.2, 160.9, 194.4; IR (KBr): ν 3499, 3139, 3026, 1686, 1663, 1609, 1530, 1463; ESI-MS: m/z 338.8 (M^++1), 676.9 ($2M^+$+1), 336.8 (M^-−1), 675.0 ($2M^-$−1).

4.3.10. 2-(4,5-Dihydroxy-2-methylphenyl)-1-(4-methoxyphenyl)-2-(tetrahydropyrimidin-2(1*H*)-ylidene)ethanone (3j). Yield: 40%; mp: 224–225 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.78 (t, $J = 4.4$ Hz, 2H, CH_2), 1.86 (s, 3H, CH_3), 3.17-3.33 (m, 4H, CH_2), 3.64 (s, 3H, OCH_3), 5.27 (s, br, 1H, NH), 6.35 (s, 1H, Ar–H), 6.49 (s, 1H, Ar–H), 6.57 (d, 2H, $J = 8.4$ Hz, Ar–H), 6.98 (d, 2H, $J = 8.8$ Hz, Ar–H), 8.50 (s, 2H, OH), 12.59 (s, br, 1H, NH); ^{13}C NMR (100 MHz, DMSO-d_6): $\delta\delta$ 19.6, 20.5, 38.6, 55.3, 92.2, 112.4, 117.9, 121.8, 127.6, 129.4, 130.0, 137.2, 143.4, 144.5, 158.6, 159.3, 180.8; IR (KBr): ν 3446, 3407, 2966, 2928, 2865, 1600, 1578, 1510, 1488; ESI-MS: m/z 354.8 (M^++1), 352.7 (M^-−1).

4.3.11. (*E*)-3-{4,5-Dihydroxy-2-[2-oxo-2-phenyl-1-(tetrahydropyrimidin-2(1*H*)-ylidene]ethyl}phenylacrylic acid (3k). Yield: 20%; mp: 203–204 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.80 (t, $J = 5.2$ Hz, 2H, CH_2), 3.17-3.36 (m, 4H, CH_2), 5.07 (s, br, 1H, NH), 5.89 (d, $J = 15.6$ Hz, 1H, CH=CH), 6.43 (s, 1H, Ar–H), 6.90-6.93 (m, 2H, Ar–H), 6.94 (s, 1H, Ar–H), 6.98-7.01 (m, 3H, Ar–H), 7.54 (d, $J = 16.0$ Hz, 1H, CH=CH), 12.41 (s, br, 1H, NH); ^{13}C NMR (100 MHz, DMSO-d_6): δ 20.3, 37.9, 39.4, 90.9, 113.3, 122.1, 126.2, 127.2, 127.5, 127.6, 128.3, 131.1, 144.7, 145.2, 148.3, 159.3, 168.7, 182.6; IR (KBr): ν 3422, 1605, 1508, 1448; ESI-MS: m/z 380.7 (M^++1), 378.7 (M^-−1).

4.3.12. (*E*)-3-{4,5-Dihydroxy-2-[2-oxo-2-*p*-tolyl-1-(tetrahydropyrimidin-2(1*H*)-ylidene)]ethyl}phenylacrylic acid (3l). Yield: 76%; mp: 209–210 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.78 (t, $J = 4.8$ Hz, 2H, CH_2), 2.14 (s, 3H, CH_3), 3.15-3.33 (m, 4H, CH_2), 5.69 (s, br, 1H, NH), 5.90 (d, $J = 16.0$ Hz, 1H, CH=CH), 6.43 (s, 1H, Ar–H), 6.78-6.83 (m, 4H, Ar–H), 6.97 (s, 1H, Ar–H), 7.56 (d, $J = 16.0$ Hz, 1H, CH=CH), 9.37 (s, br, 2H, OH), 12.46 (s, br, 1H, NH); ^{13}C NMR (100 MHz, DMSO-d_6): δ 20.4, 21.1, 38.6, 90.8, 113.4, 115.1, 122.0, 127.4, 127.7, 127.8, 131.4, 136.3, 141.9, 143.8, 145.1, 148.3, 159.3, 168.6, 182.5; IR (KBr): ν 3430, 3337, 1683, 1605, 1306; ESI-MS: m/z 394.8 (M^++1), 416.8 (M^++Na), 392.7 (M^-−1).

4.3.13. (*E*)-3-{4,5-Dihydroxy-2-[2-oxo-2-(4-methoxyphenyl)-1-(tetrahydropyrimidin-2(1*H*)-ylidene)]ethyl}phenylacrylic acid (3m). Yield: 25%; mp: 216–217 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.78 (t, $J = 5.2$ Hz, 2H, CH_2), 3.20-3.32 (m, 4H, CH_2), 3.62 (s, 3H, OCH_3), 5.60 (s, br, 1H, NH), 5.92 (d, $J = 16.0$ Hz, 1H, CH=CH), 6.43 (s, 1H, Ar–H), 6.55 (d, $J = 8.8$ Hz, 2H, ArH), 6.89 (d, $J = 8.8$ Hz, 2H, ArH), 6.99 (s, 1H, Ar–H), 7.54 (d, $J = 16.0$ Hz, 1H, CH=CH), 10.05 (s, br, 2H, OH), 12.50 (s, br, 1H, NH); ^{13}C NMR (100 MHz, DMSO-d_6): δ. 20.4, 38.0, 55.3, 90.6, 112.5, 113.5, 114.1, 115.4, 122.0, 127.4, 129.3, 131.5, 131.7, 137.1, 143.6, 145.2, 148.5, 158.5, 159.3, 168.8, 181.8; IR (KBr): ν 3551, 3414, 1663, 1637; ESI-MS: m/z 410.9 (M^++1), 432.8 (M^++Na), 4.8.8 (M^-−1).

4.3.14. 1-(4-methylphenyl)-2-(3,4-dihydroxy-5-methoxyphenyl)-2-(tetrahydropyrimidin-2(1*H*)-ylidene)ethanone (3n). Yield: 59%; mp: 194–195 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 1.84 (s, 2H, CH_2), 2.33 (s, 3H, CH_3), 3.34-3.36 (d, 4H, CH_2), 3.72 (s, 3H, OCH_3), 6.32 (s, br, 1H, NH), 6.46 (s, 1H, Ar–H), 6.54 (s, 1H, Ar–H), 7.30 (d, $J = 7.6$ Hz, 2H, Ar–H), 7.86 (d, $J = 8.0$ Hz, 2H, Ar–H), 8.86 (s, br, 1H, OH), 9.18 (s, br,1H, OH), 9.57 (s, br, 1H, NH) ^{13}C NMR (100 MHz, DMSO-d_6): δ 18.2, 21.6, 39.2, 55.1, 56.4, 105.3, 110.8, 121.8, 129.5, 129.9, 132.9, 135.4, 145.0, 146.8, 149.5, 161.1, 193.5; IR (KBr): ν 3453, 1683, 1662, 1616, 1536, 1456; ESI-MS: m/z 354.7 (M^++1), 352.7 (M^-−1).

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