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Two-electron phenolic oxidations using phenyliodonium dicarboxylates

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Abstract—Phenolic oxidations by $PhI(OCOR)_2$ are reviewed. Consideration is given to the mechanisms of the reactions and to the differing consequences of inter- and intra-molecular nucleophilic attack on the intermediate phenyloxenium ions.

1. Introduction

1.1. General considerations

One-electron oxidations of phenols are generally agreed to be the favoured mode of biochemical oxidation particularly for the large scale production of lignin[1] as well as for lignans,[1] tannins,[2] plant and insect pigments,[3] some antibiotics,[3] and many alkaloids.[3] One-electron oxidations involving a wide variety of metal ions[4] are well known and widely used (see Refs. 3,5,6,9,12–27 in Ref. 5). Electrochemical methods have also been used to study one-electron phenolic oxidations. In those cases one- and two-electron processes can be delineated unequivocally.[6–9] In most cases the reactions are non-specific and low-yielding, due to the variety of processes that $ArO^{\cdot}$, **1**, may undergo. These include homolytic coupling, radical insertion and quinone-methide formation, each being available to all of the many forms of the radicals.[10,11] Two-electron oxidation of phenols to give ArO^+, **2** has been less well explored. Some aryloxenium ions have been electrochemically generated[12,13] and studied. Some are stable enough to be isolated.[14]

Three possible methods for the chemical production of **2** have been proposed[4] and are shown in Eqs. (1)–(3). Examples of Eq. (1) in which X=NHOTos[15] and SR[16] are known, though somewhat severe conditions are required for dissociation to occur. Compounds **4** in which X=$S(Pr^i)NR_2$,[17] $S(Tol)NR_2$[17] and SMe_2[18] have been used and recently **4** ($X=SPh_2$) has been introduced to overcome the disadvantages of rearrangement when $X=SMe_2$.[4] Thermal decomposition of **4**, $X=NC_5H_5$ yields **2** which, in the cases that the aryl groups lack electron-withdrawing substituents, give only C–C bonds on nucleophilic attack.[19]

Eq. (3) has been implicated in oxidations by a variety of metals including Tl(III),[20] Cu(II),[21] Pb(IV),[22] and Cr(VI).[23]

$$\mathrm{ArOH} \longrightarrow \underset{\mathbf{3}}{\mathrm{ArOX}} \longrightarrow \underset{\mathbf{2}}{\mathrm{ArO^+}} + \mathrm{X^-} \quad (1)$$

$$\mathrm{ArOH} \longrightarrow \underset{\mathbf{4}}{\mathrm{ArOX^+}} \longrightarrow \underset{\mathbf{2}}{\mathrm{ArO^+}} + \mathrm{X} \quad (2)$$

$$\mathrm{ArOH} \longrightarrow \underset{\mathbf{5}}{\mathrm{ArOX[N]}} \longrightarrow \underset{\mathbf{2}}{\mathrm{ArO^+}} + \mathrm{X[N\text{-}2]}$$

(X is a heteroatom capable of a ready change of valency from N to N-2) (3)

The advantages for chemical syntheses of **2** over **1** have been discussed.[4,24] These advantages may be enumerated as follows. (i) If **2** is produced by a dissociative mechanism as in Eqs. (1)–(3) then, if X is attached to any particular hydroxyl group, subsequent reactions are specific to that hydroxyl group. (ii) Although radicals **1** would be expected to dimerise mainly by C–O–C bond formation, aryloxenium ions **2** would interact with uncharged species by C–C formation,[24] a prediction that has been verified.[19] (iii) Although it is simple for **1** to react with neutral species as well as other radicals, aryloxenium ions **2** cannot readily react with each other thus dramatically lowering the number of potential products. (iv) A benzylic proton can be lost from appropriately substituted **2** to yield quinone-methides ready for substitution,[25] cyclisation[25,26] and rearrangement.[27,28] *For Eqs. (1)–(3) to be successful the choice of nucleofugal group is of overwhelming importance and here we consider the case of X=PhI(III)OCOR.*

Keywords: phenol oxidation; phenyliodonium dicarboxylates; cyclohexadienones; cyclisations.

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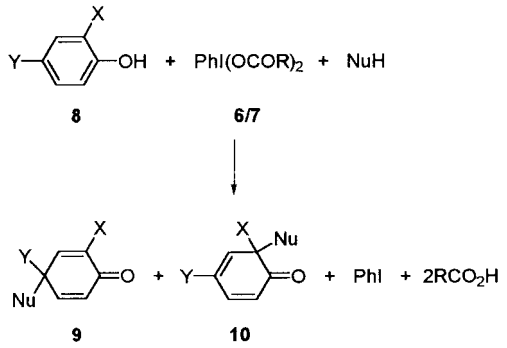


Scheme 1.

1.2. Scope of this review

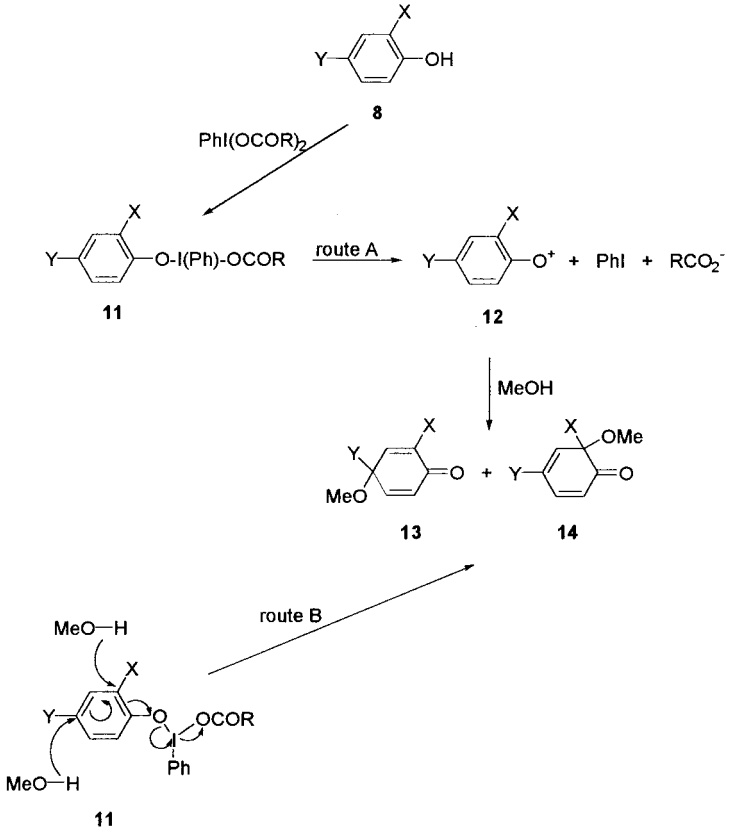
This paper deals only with phenolic oxidation with phenyliodonium diacetate (PIDA) **6** and phenyliodonium *bis*-(trifluoroacetate) (PIFA) **7** and it emphasises the work of our group. It does not deal with the further chemistry,[29] such as epoxidation[30a] and Diels–Alder reactions[30b,44] of the cyclohexadienones produced by the oxidation, nor does it survey the rich chemistry of hypervalent iodine compounds.[31] Indeed Ref. 32 lists 24 reviews on the topic since 1966.

2. Mechanism of phenolic oxidation by $PhI(OCOR)_2$

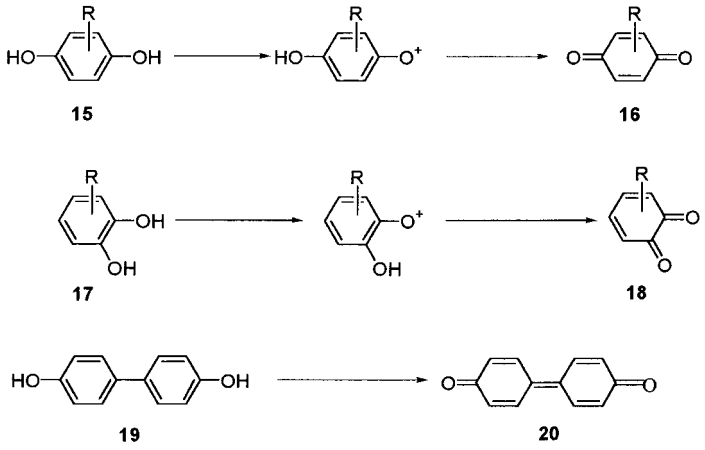
The overall reaction is shown in Scheme 1. The first point to note is that the by-products are simply acetic or trifluoroacetic acid plus iodobenzene, the latter being readily recycled.[32,33] This offers significant environmental advantages over reagents such as $Pb(OAc)_4$ and $Tl(ONO_2)_3$. The next point is to question the mechanism by which **6**/**7** converts phenols **8** into products **9** and **10**, products that are typical for two-electron oxidations of phenols.[34]

There are two main possibilities for the pathway involved, as shown in Scheme 2 (NuH=MeOH). In route A the intermediate **11**, common to both pathways, dissociates to give solvated phenoxenium ion **12** which, depending on the nature of X and Y is attacked at C-4 or C-2 or both. In route B there is no dissociation prior to attack by methanol and no ionic intermediate.

We favour route A, and have used its formalism throughout, for the following reasons. (i) The phenyliodono group is a remarkable nucleofuge with a leaving ability 8×10^5 times that of a triflate group.[35] (ii) Mulliken charge calculations of a series of 2-, 3- and 4-monosubstituted phenyloxenium ions have been carried out.[34] The charge distributions very accurately predict the position of nucleophilic substitution. Thus 4-alkyl- and 4-alkoxy-phenols substitute at C-4 even when that position is highly hindered by double substitution at C-3 and C-5. When Y=H and X=OMe substitution is at C-2 even though C-2 is the most hindered position, which is exactly as predicted for the highly ionic intermediate **12**. (iii) Use of either homochiral iodonium compounds or homochiral solvents gave no trace of diastereo- or enantioselectivity in the products.[34] This negative evidence is also



Scheme 2.



Scheme 3.

completely in accord with the intermediacy of solvated aryloxenium ions in phenolic oxidations by $PhI(OCOR)_2$.

3. Oxidations of phenols

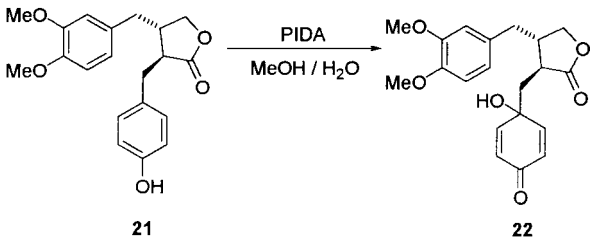
3.1. Oxidations involving proton loss

Pelter and Elgendy showed that PIDA oxidises both *para*- and *ortho*-hydroquinones **15** and **17** to the corresponding quinones **16** and **18**.[4,36] The reaction conditions are mild (20°C/MeOH) and the yields between 91–100%. Thus *ortho*-quinones were isolated in high yields despite the ease with which they undergo Diels–Alder reactions (Scheme 3). There was no evidence of attachment of methanol and evidently proton loss is faster than attack by an external nucleophile. Extended quinol **19**, which gave complex mixtures with Me_2S–NCS and did not react at all with Koser's reagent, gave an excellent yield of extended quinone **20** with PIDA (Scheme 3).

4. Oxidation of phenols with attack by an external nucleophile

4.1. Water as external nucleophile

It has been shown[37] that, in PIDA oxidations, water is a more effective nucleophile than methanol. Thus in the oxidation of **21** with PIDA in a mixture of $MeOH/H_2O$ (9:1) only the hydroxy compound **22** was isolated in 91% yield (Eq. (4)).



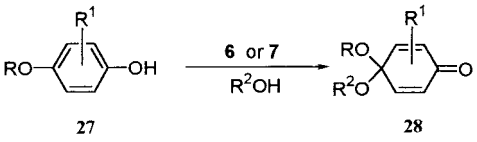
(4)

This reaction illustrates two further points of interest. The first is that although **6** and **7** readily oxidise phenolic ethers,[32] the oxidation of phenols is much faster. The second is that the conditions tolerate lactone functionality and do not affect stereogenic centres. Similarly amino-acetal functions are also kept intact.[29]

In the case of 4-unsubstituted phenols, double oxidation in water occurs to give *p*-quinones,[38] a reaction in which **6** rather than **7** is the preferred oxidant. Functionality tolerance includes benzylic OH,[38] the pyridine ring,[39] the indole ring system[40] and aliphatic amine derivatives.[41]

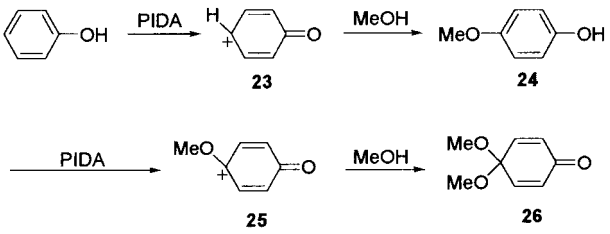
4.2. Alcohols as external nucleophiles

The reaction of phenol with PIDA in methanol does not yield 4-methoxyphenol **24** even when only one equivalent of PIDA is used. This is not surprising as the phenoxenium ion **25** would be stabilised by a factor of at least 2000 with respect to the simple ion **23** (Scheme 4). Use of two equivalents of PIDA gave the useful synthon[29] **26** directly and in 68% isolated yield.[4] 4-Alkoxyphenols **27** yield quinone ketals **28** directly and in good yields (Eq. (5)).[4,36,42]

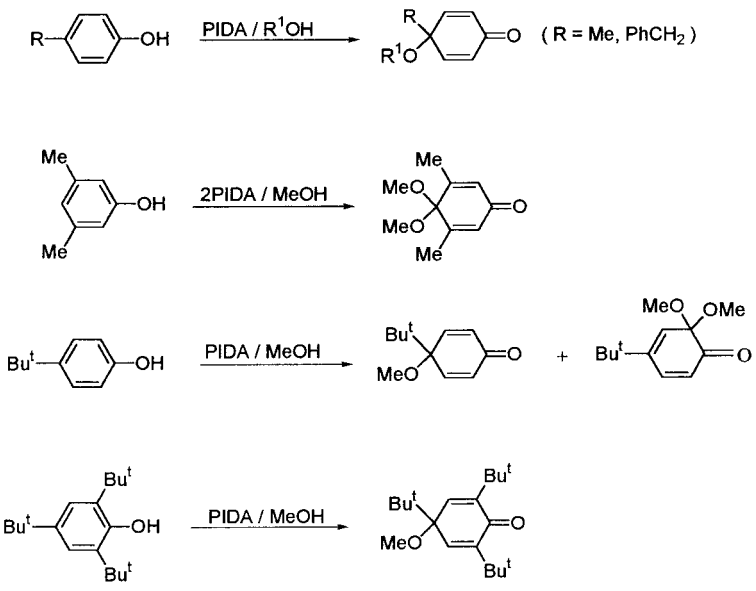


(5)

The many variants of this reaction constitute one of the most valuable of the phenolic oxidation reactions. When 3- or 5-alkoxy groups are present in addition to the 4-alkoxy group then the nucleophile enters at C-4 only.[42] However, in agreement with calculations, phenols **29** having a 2-alkoxy group oxidise to give 2,2-dialkoxy-3,5-cyclohexadienones

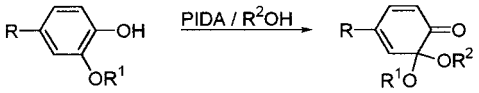


Scheme 4.



Scheme 5.

30 (Eq. (6)).[42,43] This reaction has been well used in anthraquinone[43] and lignan synthesis.[44]



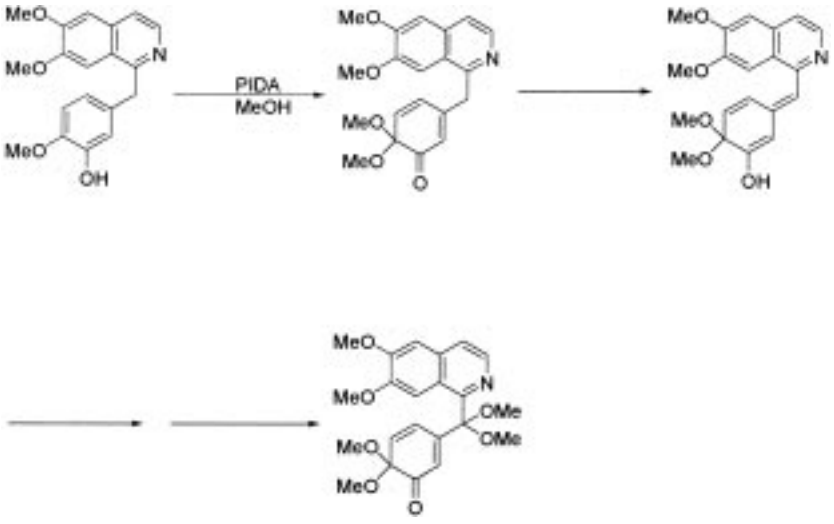
29 **30** (6)

When alkyl phenols are oxidised the major products are invariably the 4-substituted 2,5-dienones (Scheme 5). The double oxidation of 3,5-dimethylphenol proceeds at C-4 only,[4,36] despite the hindrance at this position. However steric hindrance *can* play a role as in the case of 4-*t*-butylphenol but when the hindrance at C-4 is the same as at C-2 and C-6 as in 2,4,6-tri-*t*-butylphenol, oxidation gave C-4 substitution only.[4,36]

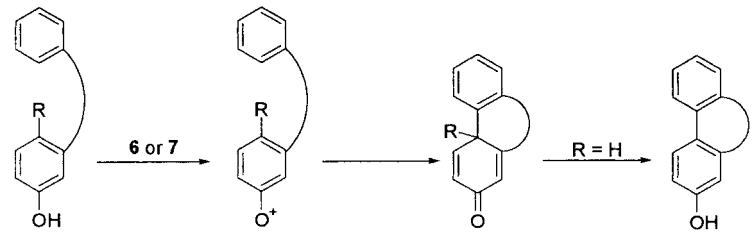
Both methyl 3-(4-hydroxyphenyl)propionate and *N*-acetyl-L-tyrosine ethyl ester are oxidised by **6** with substitution at C-4.[43] The reagent therefore tolerates ester and amide groups. Double bonds may also be tolerated by the reagents except where appositely placed for cyclisation[12,45] (cf. Eq. (12)). Sometimes very interesting products may result from quinone-methide formation followed by addition[46] (Scheme 6).

2-Naphthols are oxidised by PIDA/MeOH to yield 1,1-dimethoxynaphthalenones.[43,47] The reason for substitution exclusively at C-1 has not been the subject of MO calculations.

Not all phenols react as outlined above. Some phenols substituted with electron withdrawing groups may give products arising from aryliodination when oxidised with PIDA in methanol.[48]



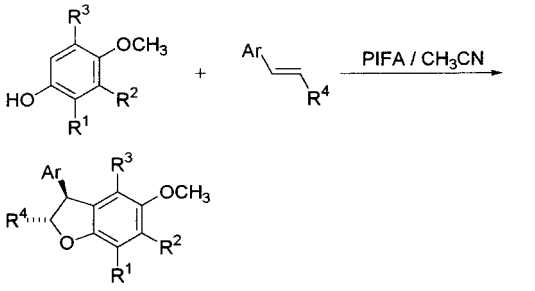
Scheme 6.



Scheme 7.

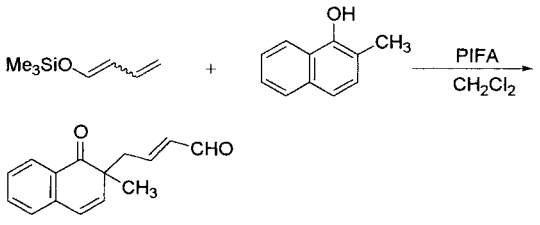
5. Reactions with alkenes

Hypervalent iodine oxidation of phenols in the presence of alkenes may result in new carbon–carbon bond formation.[49,50] The reaction has considerable synthetic potential as emphasised by the intramolecular example given in Eq. (12). It is interesting that 2-naphthol reacts solely at C-1, as in the reaction with methanol, suggesting similar intermediates. An example of an alkene acting as an external nucleophile is given in Eq. (7).[49]



(7)

Further examples include the reactions of allylsilanes and 1-silyloxydienes with 2-substituted phenols and 2-substituted α-naphthols. In the latter case, even when the 2-substituent is an alkyl group, substitution occurs in the 2-position (Eq. (8)).[50]



(8)

6. Attack by fluoride

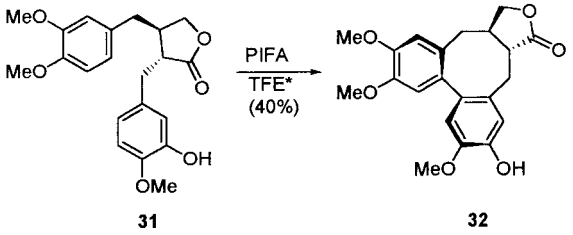
4-Alkylphenols react with PIDA in the presence of pyridinium polyhydrogen fluoride to give 4-alkyl-4-fluoro-2,5-cyclohexadienones.[51] 2-Hydroxytetralone behaves similarly and the method has been used to produce 10-fluoroestrones.[51]

7. Cyclisation reactions

7.1. Cyclisations involving C–C bond formation

Oxidative coupling reactions, in which an activated aromatic ring is attacked intramolecularly by a second, nucleophilic, aromatic ring, are useful reactions for synthesising natural products containing a biaryl unit. Two possible types of reaction are shown in Schemes 7 and 8, depending upon whether the original linkage between the two rings is connected at the *meta* or *para* position of the phenol.

An example of the type of reaction shown in Scheme 7 is provided by our own work on the synthesis of dibenzocyclooctadiene derivatives.[52,53] Oxidation of the *m*-hydroxybenzylbutyrolactone derivative **31** yielded the isostegane derivative **32** (Eq. (9)).[53] A higher yield (72%) was obtained when ruthenium dioxide was used as the oxidising agent.[53,54]

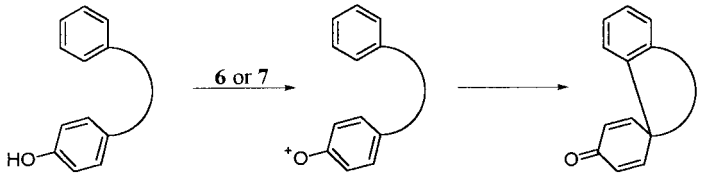


31 **32**

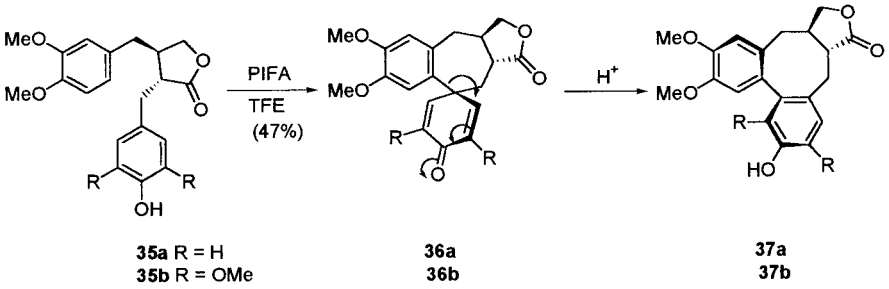
(9)

* TFE = 2,2,2-trifluoroethanol

An example of the type of reaction shown in Scheme 8 is the preparation of salutaridine derivatives by PIDA or PIFA

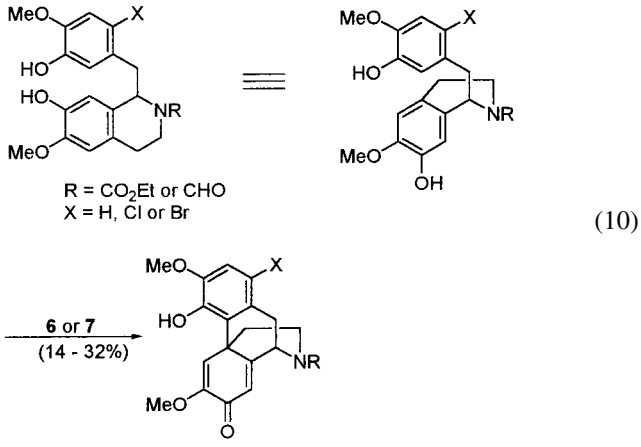


Scheme 8.



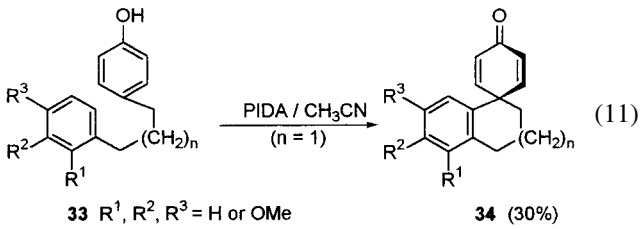
Scheme 9.

oxidation of 1-benzyltetrahydroisoquinolines (Eq. (10)).[55]



(10)

The majority of known biaryl coupling reactions are of this type and involve starting materials in which the original linkage between the two rings is attached to the *para* position of the phenol. This invariably leads to a spirodienone as the first-formed product and it is usually the further rearrangement of this compound that dictates the ultimate outcome of the reaction sequence. A simple example of such a reaction is shown in Eq. (11).[56] The yields of the spirodienones **34** (n=1) were low (30%) and their further rearrangement was apparently not investigated. It is interesting to note that when a higher homologue of **33** (n=2) was used, no cyclisation was observed.[52,53]



(11)

However, when the mobility of the linking group was restricted by the inclusion of a *trans*-butyrolactone moiety, as in **35a**, then the spirodienone **36a** was obtained (Scheme 9). Longer reaction times, or treatment of **36a** with acid, brought about rearrangement to give mainly the isostegane derivative **37a** (plus a small amount of the stegane isomer **38a**, see below).[52,53] It is of interest that this reaction involves an aryl migration, in contrast to the corresponding reactions of the naturally occurring eupodienones which, at least in some cases, proceed by alkyl migration.[57]

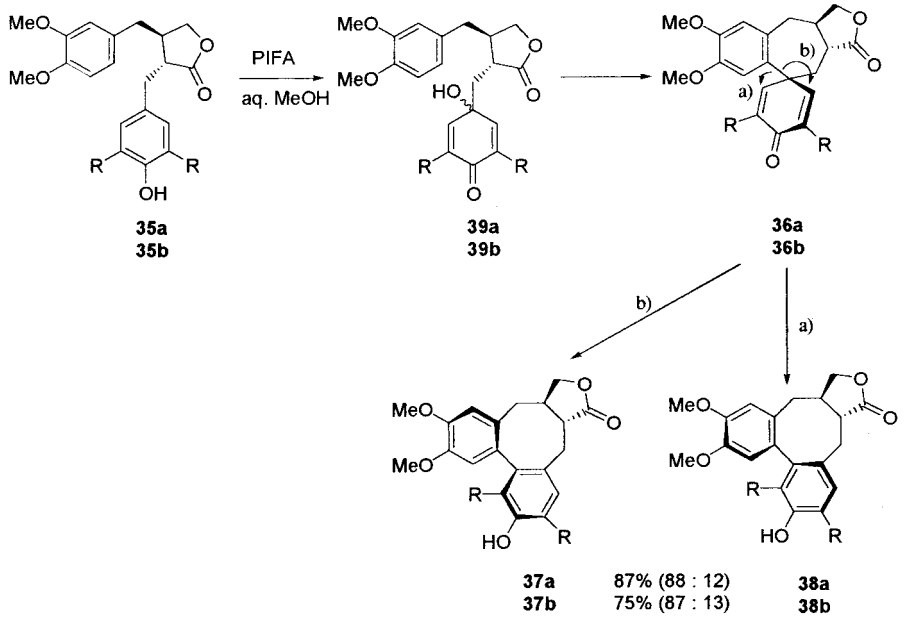
Higher yields of **37a** were obtained by treating **35a** with PIFA in aqueous methanol, followed by treatment with TFA. Under these conditions **37a** was obtained, along with some of the corresponding stegane isomer (**38a**), in a combined yield of 87% (**37a**:**38a**=88:12) (Scheme 10).[37] Similarly, **35b** was converted under these conditions into a mixture of **37b** and **38b** in 75% yield (**37b**:**38b**=87:13). These reactions are thought to involve initial formation of a 4-hydroxycyclohexadienone **39**, followed by cyclisation to give the spirodienone **36**, and then rearrangement to the dibenzocyclooctadienes **37** and **38**.

In the case of the 4-hydroxy-3-methoxybenzylbutyrolactone **40** two spirodienones, **41** and **42,** can in principle be formed (Scheme 11). Only one of these, **41**, has been isolated, but the fact that two rearranged products, **43** and **44**, were obtained in a 1:1 ratio when the reaction was carried out in trifluoroethanol, is consistent with the conclusion that both **41** and **42** are present, and that **41** rearranges regio- and stereo-selectively to give **43**, and **42** rearranges with equal selectivity to give **44**. This conclusion is supported by the observation that treatment of **41** with perchloric acid gives a quantitative yield of **43**. Furthermore, it is consistent with the proposal that in both cases the aryl group migrates to the most electron deficient centre, and that migration to give the isostegane configuration takes place most easily (**42**→**44**, cf. **36**→**37**). When **40** is treated with PIFA in aqueous methanol, followed by treatment with TFA, **43** and **44** were obtained in 81% yield and in a 1:1 ratio.

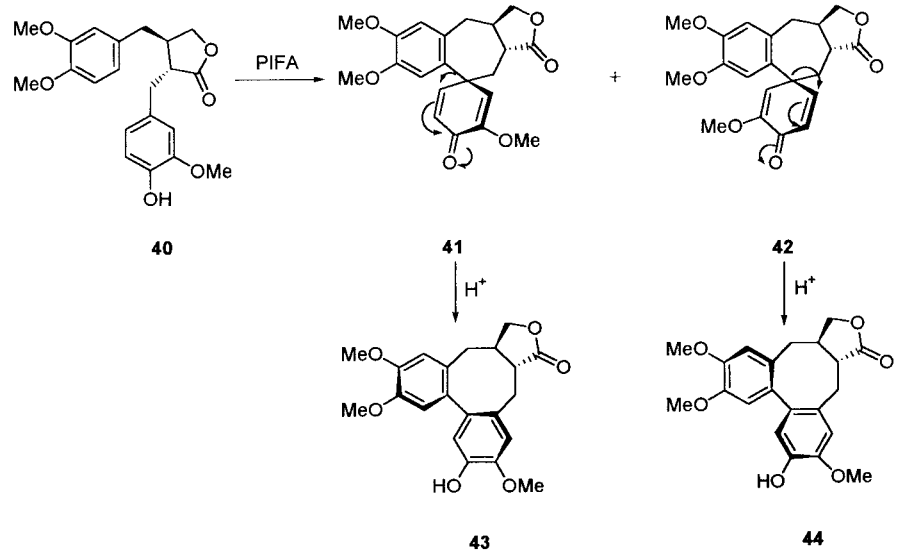
Compounds **35a** and **35b** are symmetrically substituted in ring B so that each can yield only one spirodienone intermediate. For **40**, which can give two spirodienone intermediates, **41** and **42**, the migration process appears to be controlled by the production of those intermediates, the subsequent migration being by an aryl group to the most electron deficient and least hindered position of the dienones.

The methodology given above for the synthesis of steganes has been adapted to their chiral synthesis by using 5-menthyloxybutenolide as starting material rather than butenolide itself.[58]

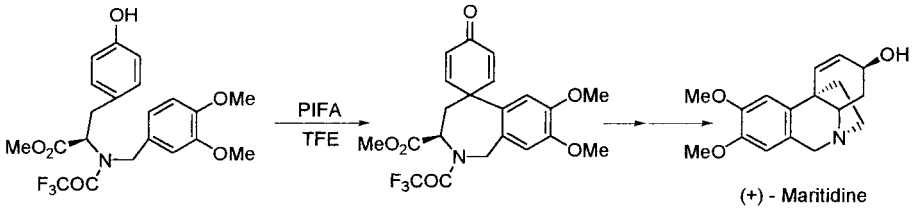
Kita et al. have synthesised a number of *Amaryllidaceae* alkaloids in an analogous fashion using intramolecular cyclisation to form a seven-membered heterocyclic ring (Scheme 12).[59,60] Cyclisations involving phenoxenium ions are also known in which the attacking nucleophile is a carbon–carbon double bond. Thus 4-(2-alkenyl-aryl)-phenols have been cyclised to give spirodienones in yields



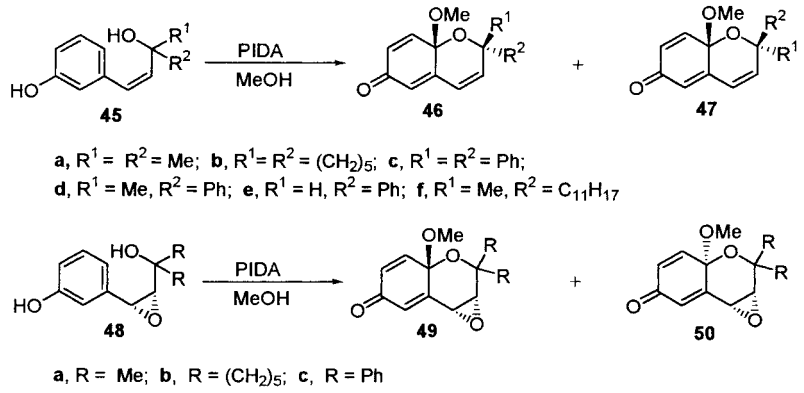
Scheme 10.



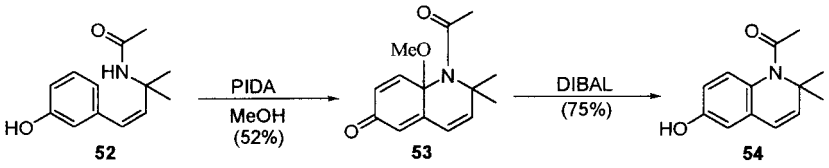
Scheme 11.



Scheme 12.

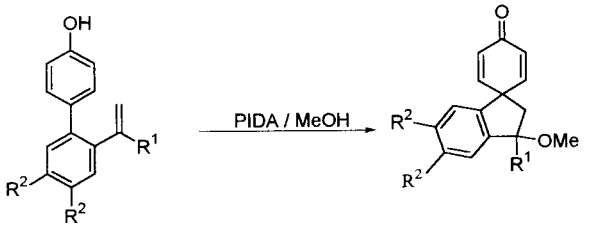


Scheme 13.



Scheme 14.

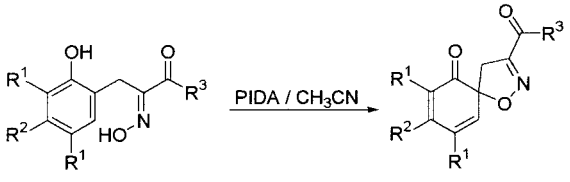
of up to 92% (Eq. (12)).[12] In this case it was shown that the same products are formed by electrochemical oxidation, and this provides compelling evidence in favour of the intervention of phenoxenium ions in these cyclisation reactions.



(12)

7.2. Other cyclisations

Cyclisations involving phenoxenium ions are also known in which the attacking nucleophile is a hydroxy group. The formation of lactones by cyclisation of carboxylic acids was early demonstrated[42] and more recently spiroisoxazolines have been synthesised from phenolic oxime acid derivatives (Eq. (13)).[61]

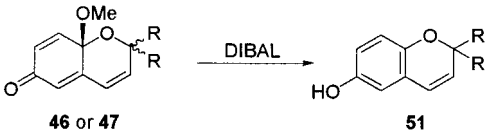


(13)

R^1 = H, R^2 = OMe, R^3 = OMe	40%
R^1 = H, R^2 = OMe, R^3 = $NH(CH_2)_3OMe$	46%
R^1 = Br, R^2 =H, R^3 = OMe	76%
R^1 =Br, R^2 = H, R^3 = $NH(CH_2)_3OMe$	64%

We have devised a new synthesis of chromene derivatives which involves two-electron oxidation of *meta*-substituted phenols **45** containing a *cis*-allylic alcohol group (Scheme 13).[62] The conformational constraint imposed by the carbon–carbon double bond was found to be essential, since the dihydro-derivative of **45** did not undergo cyclisation. The necessary constraint could also be provided by an epoxide group as in **48**.

DIBAL reduction of the chromenones **46** or **47** gave the corresponding chromenes **51** (Eq. (14)).[62] Oxidation of the chromenes in methanol regenerated the chromenones, suggesting that **51** may be an intermediate in the formation of **46** and **47** from **45**. We have also extended this methodology to produce a 1,2-dihydroquinoline derivative (Scheme 14).[63] Thus, treatment of the allylic amide **52** with two equivalents of PIDA in methanol gave the dienone **53** which on reduction with DIBAL gave **54**.



(14)

8. Conclusion

Phenyliodonium dicarboxylates readily and in high yields convert phenols into cyclohexadienones. In some respects the transformation is the oxidative analogue of the Birch reduction inasmuch as it converts simple aromatic compounds into highly functionalised cyclohexene derivatives which are eminently suitable for further elaboration. The intermediate phenyloxenium ions may be attacked by external nucleophiles or by internal nucleophiles. The latter reactions lead to a variety of cyclisation products.

9. Experimental

9.1. Preparation of the spirodienone 36a[54]

Compound **35a** (1.00 g, 2.92 mmol) was dissolved in dry trifluoroethanol (TFE) (16 ml) under nitrogen. To the stirred solution was added PIFA (1.51 g, 3.51 mmol, 1.2 mol equiv.) dissolved in dry TFE (13 ml), via syringe and stirring was continued at rt for 1 h. After this time, the reaction mixture was neutralised by addition of powdered $NaHCO_3$, filtration and concentration in vacuo. The residue was dissolved in EtOAc and filtered, and the filtrate was evaporated and the residue purified by flash chromatography on silica using gradient elution with CH_2Cl_2/EtOAc. Elution with a 4:1 mixture afforded **36a** (0.466 g, 47%), which crystallised from EtOAc as colourless crystals mp 193–194°C. Found: C, 70.36; H, 5.94. $C_{20}H_{20}O_5$ requires C, 70.59; H, 5.88; ν_{max} (KBr): 1670 cm^{-1} (C═O), 1780 cm^{-1} (γ-lactone); λ_{max} (MeOH), 208.8 nm (ϵ, 53 574), 235.1 nm (ϵ, 36 137), 279.7 nm (ϵ, 5 731); see Ref. 54 for ^1H and ^{13}C NMR data; *m/z* (e.i.) 370 (M^+, 13%); Found: M^+ 340.1310. $C_{20}H_{20}O_5$ requires 340.1311.

9.2. Preparation of rel(1a,12aR_a,6*R*,7*R*)-11-hydroxy-6-hydroxymethyl-2,3-dimethoxy-5,6,7,8-tetra-hydrodibenzo[1a,4a:8a,12a] cyclooctene-7-carboxylic acid lactone (37a) and rel(1a,12aS_a,6*R*,7*R*)-11-hydroxy-6-hydroxymethyl-2,3-dimethoxy-5,6,7,8-tetrahydrodibenzo-[1a,4a:8a,12a] cyclooctene-7-carboxylic acid lactone (38a)[37]

The phenol **35a** (0.5 g, 1.46 mmol) was dissolved in a methanol–water mixture (9:1; 50 cm^3) and PIFA (3.14 g, 7.3 mmol), dissolved in the same solvent mixture (20 cm^3), was added slowly to the stirred solution. The resulting solution was stirred for 15 min after which the solvent was rapidly removed by evaporation on an oil pump to yield a red gum (3.49 g). The gum was dissolved in EtOAc (20 cm^3) and the solution washed with water (3×30 cm^3), dried ($MgSO_4$) and filtered. Neutral silica (10 g) was added to the solution and the solvent removed by oil pump. The resulting silica was then placed on top of a neutral silica column. Elution with light petroleum removed all of the iodobenzene formed during the reaction and elution with a mixture of light petroleum–EtOAc (3:7) gave a mixture of products and left any unchanged PIFA on the column. The fractions containing the products were combined and the solvent removed to yield an orange gum (0.48 g) which was dissolved in methanol (20 cm^3). TFA (20 cm^3) was added to the solution with constant stirring and the mixture left for 6 h. After this time the reaction had gone to completion and the solvents were removed by evaporation under reduced pressure. The residue was taken into EtOAc (30 cm^3) and the solution washed with water (3×30 ml), dried ($MgSO_4$), filtered and evaporated. The resulting residue contained only a mixture of the desired products **37a** and **38a** (0.44 g, 87%) and HPLC analysis showed a ratio of 88:12 for **37a** to **38a**. Repeated crystallisation from EtOAc–light petroleum gave colourless crystals of **37a** (0.365 g), mp 187–189°C. Found: C, 70.43; H, 6.09. $C_{20}H_{20}O_5$ requires C, 70.59; H, 5.88; ν_{max} (KBr): 1745 cm^{-1} (γ-lactone), 3400 cm^{-1} (OH); λ_{max} (MeOH), 216.8 nm (ϵ, 44 038), 280.8 nm (ϵ, 10 934); see Ref. 54 for ^1H and ^{13}C NMR data; *m/z* (e.i.) 340 (M^+, 100%), and **38a** (0.047 g), mp 184–186°C, see Ref. 54 for ^1H and ^{13}C NMR data.

9.3. Preparation of 6-hydroxy-8a-methoxy-2,2-dimethyl-2H, 6H-dihydrochromen-6-one (46a)[62]

To a stirred solution of **45a** (2.015 g, 0.0113 mol) in dry methanol (10 ml) was added PIDA (7.283 g, 0.0226 mol), and stirring continued for 45 min before concentration under vacuum. The products were immediately separated by flash chromatography on neutral silica using CH_2Cl_2, to give the product (**46a**) (1.934 g, 0.0094 mol, 83%) as a brown oil. ν_{max} (cm^{-1}), 2977, 2828 (C–H), 1667 (C═O); λ_{max} (MeOH), 215.5 nm (ϵ, 22 982), 313.6 nm (ϵ, 7 532); see Ref. 62 for ^1H and ^{13}C NMR spectra; *m/z* (e.i.), 206 (M^+, 4%), 191(8), 175(29), 164(91), 103(20), 91(47), 77(46), 43(100); Found: M^+ 206.0943. $C_{12}H_{14}O_3$ requires 206.0943.

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