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The Chemistry of 2-Oxido-3-phenyliodonio-1,4-benzoquinones: Transformation to 2-Cyclopentene-1,4-diones and Cycloadditions

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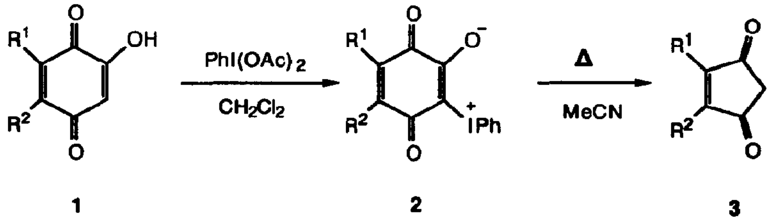
Abstract: The conversion of substituted 2-hydroxy-1,4-benzoquinones, **1**, to 2-cyclopentene-1,4-diones, **3**, is effected by thermolysis of their iodonium zwitterions, **2**. Some cycloadditions through **2** are also described.

Iodonium zwitterionic compounds constitute a fairly large family of hypervalent iodine compounds with interesting and sometimes unexpected reactivity.[1] In a previous publication we noticed the quantitative formation of 1,3-indandione upon heating of 2-oxido-3-phenyliodonio-1,4-naphthoquinone in acetonitrile.[2] We now find that this reaction can be extended also to 2-oxido-3-phenyliodonio-1,4-benzoquinones, which are converted into 2-cyclopentene-1,4-diones. Despite their simple structure, in which enolization is not favored, these diketones are not easily accessible, with the exception of the parent compound.[3] Generally, substituted 2-cyclopentene-1,4-diones may be regarded as potentially valuable building blocks for a number of natural products or compounds of complex structure; for example, Michael or Diels-Alder adducts and reduction products are of obvious synthetic utility.

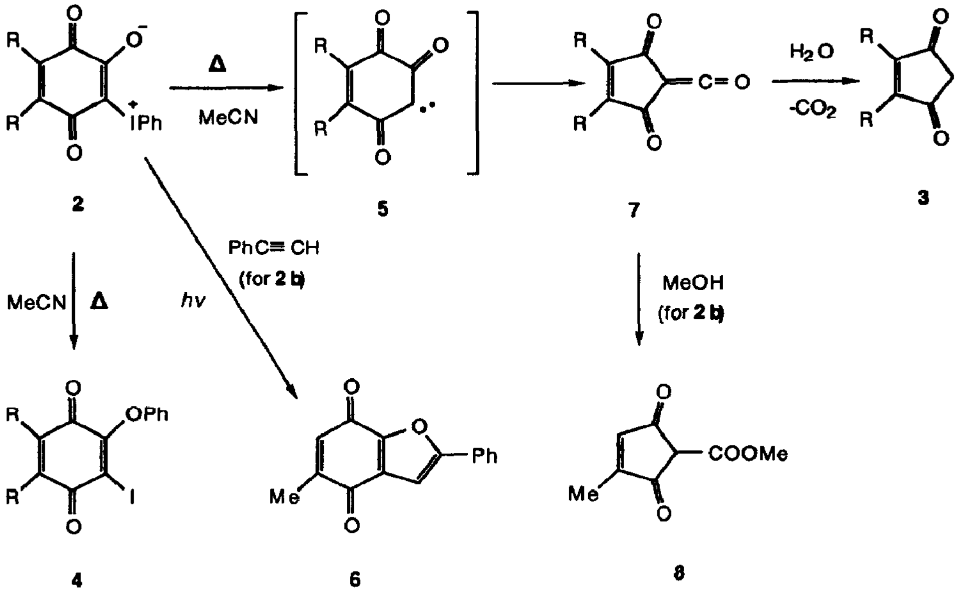
Substituted hydroquinones have been used as starting materials. These were converted into 2-hydroxy-1,4-benzoquinones, **1**, by the sequence: oxidation to 1,4-benzoquinones, acetylation and acetoxylation to 1,2,4-tris-acetoxybenzenes, hydrolysis and again oxidation to **1**, all steps in high yields[4]. Upon mixing of equimolecular amounts of **1** and (diacetoxyiodo)benzene in methylene chloride at 0 °C, the phenyliodonium zwitterions **2** precipitate and are obtained in good yields. Although they are thermally labile and cannot be recrystallized, they are reasonably stable and may be stored for a long time under refrigeration. Their identification was based on spectroscopic data and chemical reactivity; in ^{1}H-NMR they have the characteristic pattern of the PhI^+ group in the aromatic region (multiplets at 7.45 and 7.80 δ) in addition to the peaks of the corresponding hydroxyquinone moiety, while in MS peaks at 204 (PhI^+) and 77 (Ph^+) are of great intensity.



	yield %	yield %
a : R^1=H , R^2=H	(-)[5a]	60[5b]
b : R^1=H , R^2=Me	91	55
c : R^1=Me , R^2=Me	60	52
d : R^1=H , R^2=Br	(-)[5c]	29[5d]
e : R^1=H , R^2=Ph	93	85

Scheme 1

The thermolysis of **2** was carried out in refluxing acetonitrile (1 mmol in 20 ml) for 1 to 3 h, without catalyst. Column chromatography (silica gel) of the reaction products afforded **3**, in the yields indicated in Scheme 1.[6] The formation of by-products in small amounts (2-5%) was also detected, notably when concentration was sufficiently high (about 1 mmol in 4 ml). These were rearranged isomers of zwitterions **2**, i.e. 2-phenyloxy-3-iodo-1,4-benzoquinones, **4** (Scheme 2). Analogous iodoethers are known to be produced quantitatively upon thermolysis of a variety of aryliodonium zwitterions and ylides.[1,7]

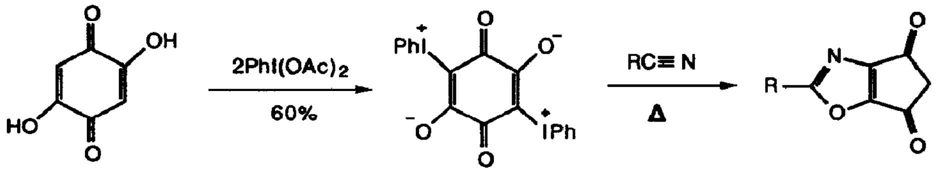


Scheme 2

A Wolff-type rearrangement must be responsible for the main transformation, **2** to **3**. In this reaction elimination of iodobenzene leads to a ketocarbene **5** which then undergoes ring-contraction and gives a ketene, **7**; this reacts with moisture from the solvent (not previously dried) and the resulting β-ketoacid spontaneously will decarboxylate to afford **3**. Indeed, when the thermolysis of **2b** was carried out in dry methanol, the ester **8** was obtained (yield 7%). All attempts to isolate **7** were unsuccessful.

A feature of iodonium zwitterions is to undergo reactions, which *formally* involve carbenoid species such as **5**, generated after elimination of iodobenzene. However, when apparent [3+2] cycloadditions are involved, with several dipolarophiles, this pathway does not seem to operate. The formation of labile iodine (III) adducts is favored in such cases,[8] especially under photolytic conditions. In order to test the potential of **2** for this kind of cycloadditions, the reaction of **2b** with phenylacetylene was examined; simple or catalytic thermolysis were not effective but under photochemical conditions the adduct **6** was obtained in 20% yield.

A double iodonium zwitterion, **10**, was obtained from 2,5-dihydroxy-1,4-benzoquinone,[9] **9** and two equivalents of $PhI(OAc)_2$ (Scheme 3). Upon thermolysis in acetonitrile, **10** gave among several non-identified products, the isoxazole derivative **11a**. Similar products (**11b**, **11c**) were formed in low yield, when propionitrile and benzonitrile were used instead of acetonitrile.[5c] In these cases, apart from the Wolff-type rearrangement which occurs from one functionality, a formal [3+2] cycloaddition between the ketocarbene and the nitrile function occurred. Such reactions have been described in rather few cases with iodine (III) precursors coming from some β-diketones.[10]



9 **10** **11**

a : R = Me (10%)
b : R = Et (5%)
c : R = Ph (5%)

Scheme 3

Preliminary experiments have shown that the reactivity of **2** can be extended to reactions with nucleophiles.

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5. a) Compound **1a** was not isolated; zwitterion **2a** was prepared directly from the reaction of 1,2,4-tris-hydroxybenzene with 2 equivalents of (diacetoxyiodo)benzene in 68% overall yield. b) Cyclo-pentenedione **3a** tends to polymerize on standing in acidic solution; column chromatography (SiO_2) is necessary immediately after the end of the reaction. c) Zwitterion **2d** was prepared from 5-bromo-1,2,4-tris-acetoxybenzene by the already described sequence, without isolating the intermediates, in 55% overall yield. d) Cyclopentenedione **3d** decomposes on column; it was purified by repeated recrystallizations from hexane. e)All new compounds were characterized by spectroscopic methods.

6. All cyclopentenediones **3**, with the exception of **3d**, have been previously obtained through lengthy routes in low yields.

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