A Novel Synthesis of *p*-Benzoquinone Ethylene Acetal

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Summary 2-Phenoxyethanol reacts with mercuric oxide and iodine in the dark to give 2-(*p*-iodophenoxy)ethanol and this product on irradiation in the presence of the mercuric oxide–iodine reagent gives mainly the ethylene acetal of *p*-benzoquinone; in contrast irradiation of 2-phenoxyethanol with the mercuric oxide–iodine reagent gave, in addition to the acetal, 2,3-dihydrobenzo-[*b*]dioxin and *p*-benzoquinone as well as starting material.

SINCE previous methods of preparation of benzoquinone acetals have been limited[1,2] and classical procedures for the preparation of benzoquinone diacetals have failed,[1,3] we are prompted to report results on the reaction of mercuric oxide–iodine reagent with 2-phenoxyethanol which gives synthetically useful yields of *p*-benzoquinone ethylene acetal. This reaction is also a further example of spiro (Ar_1-5) cyclisation[4] in which the intermediate species is trapped, and to our knowledge is the first example of this cyclisation process involving an alkoxyl radical.

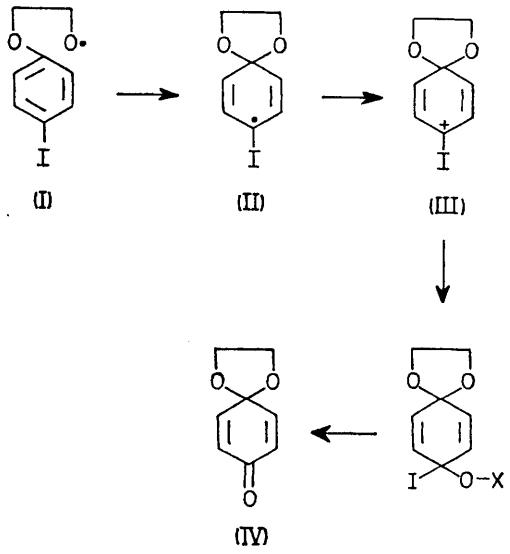
In the dark 2-phenoxyethanol is almost quantitatively converted into 2-(*p*-iodophenoxy)ethanol. This iodination on the *p*-position of an aromatic ring activated towards S_E reactions most probably occurs *via* a polar process involving I_2O[5] and not the hypoiodite since anisole was converted, in high yield, to *p*-iodoanisole with mercuric oxide and iodine. It has also been shown[6] that, in contrast to iodine monochloride,[7] *N*-iodoamides,[8] and trifluoroacetyl hypoiodites[9] in acid medium, t-butyl hypoiodite iodinates anisole slowly.

Irradiation (tungsten lamp) of 2-phenoxyethanol with mercuric oxide–iodine reagent (2M) in benzene gave 2-(*p*-iodophenoxy)ethanol (31%), 2,3-dihydro-6-iodobenzo[*b*]-dioxin (14%), 2,3-dihydrobenzo[*b*]dioxin (9%), *p*-benzoquinone ethylene acetal (34%) (IV), and *p*-benzoquinone (6%). Under the same reaction conditions 2-(*p*-iodophenoxy)-ethanol with mercuric oxide–iodine reagent (3M) gave the acetal in 84% yield. An equivalent yield was obtained from 2-phenoxyethanol when it was stirred in the dark with mercuric oxide and iodine (3M) for 4 h prior to irradiation with a tungsten lamp for 6 h.

TABLE

p-X-phenoxyethanol	Yield of 2,3-dihydro-6-halogenobenzo-[*b*]dioxin	Yield of *p*-benzoquinone ethylene acetal (IV)
X = H	14	34
X = I	8	84
X = Br	30	16
X = Cl	35	16

The cyclisation process must be due to reaction of the alkoxyl radical (I) with the iodinated aromatic ring since cyclisation only occurs on irradiation. The intermediate radical (II) cannot form the product (IV) *via* an oxygen trapping process because insufficient oxygen is present in the reaction mixture to account for the high yield of product. Further, iodine, which is an effective radical trap,[10] is present in the reaction mixture and the radical (II) would thus not be expected to react with the oxygen species present in the reaction mixture. Since the carbonyl group is present prior to workup, the carbonyl function is most likely formed from a carbocation (III) generated from the intermediate radical (II) by oxidation. Reaction of the carbocation with an oxygen species (H_2O, HOI or I_2O) followed by an elimination process would account for the formation of the carbonyl group.



We have also demonstrated, by n.m.r. spectral analysis, that 2-(*p*-bromophenoxy)- and 2-(*p*-chlorophenoxy)-ethanol are stable to mercuric oxide–iodine reagent in the dark but when irradiated produce more of the respective 2,3-dihydro-6-halogenobenzo[*b*]dioxins than the acetal (Table).

All the products have been fully characterised.

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