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From Aryliodonio-quinoline-8-olates to Arylquinolinium-8-olates by a Two Step Aryl Migration

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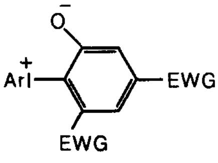
Abstract: The reaction of 4-nitro-8-hydroxyquinoline with (diacetoxyiodo)benzene affords aryliodonio-quinoline-8-olates. Thermal migration of the aryl group from iodine to oxygen and photochemical migration from oxygen to nitrogen leads to the formation of intesively coloured arylquinolinium-8-olates.

Aryliodonio phenolates **1** belong to the major class of zwitterionic iodonium compounds, the chemistry of which, as well as of other classes of hypervalent iodine compounds, has been reviewed by Varvoglis.[1] The term aryliodonio phenolates refers to 1,4 dipoles with the negative charge on the oxygen atom of a phenolic group. The presence of electron withdrawing groups, mostly nitro groups, is necessary for the stabilization of these compounds.



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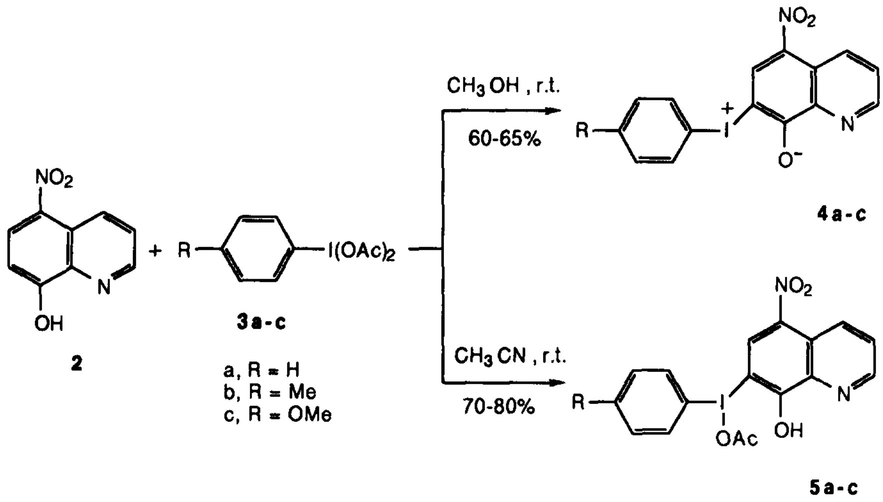
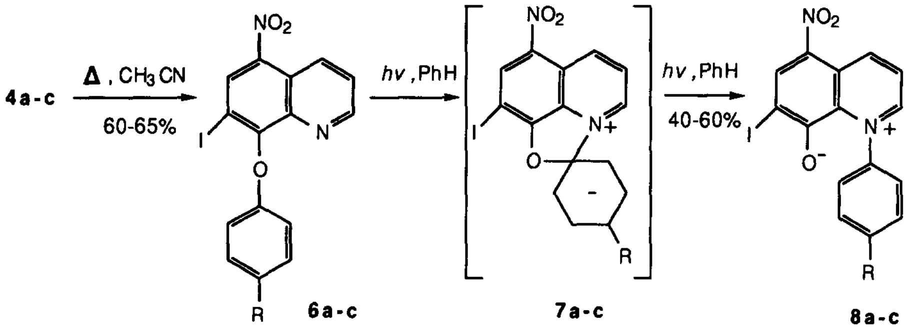
Aryliodonio phenolates react with nucleophiles and electrophiles[2] and afford cyclization products with various dipolophiles.[3] Recently we reported the formation of aryliodonio phenolates from 1,3-dihydroxy-benzene derivatives.[4]

Continuing the exploration of the chemistry of zwitterionic iodonium compounds,[5] we considered the possibility of forming aryliodonio phenolates from 8-hydroxy-quinoline (oxine) and its derivatives. Oxine, upon treatment with (diacetoxyiodo)arenes **3**, gave complicated mixtures of oxidation products, but its 5-nitro derivative **2** afforded 5-nitro-6-aryliodonio-quinoline-8-olates **4a-c**, or their acetoxy salts **5a-c**, depending on the nucleophilicity of the solvent used for the reaction (Scheme 1).



Scheme 1

Both **4** and **5** were isolated by filtration. They are fairly stable and elucidation of their structure was based on spectroscopic data and elemental analyses. Quinoline-8-olates **4** are converted to the corresponding iodo ethers **6a-c** in refluxing acetonitrile (Scheme 2). This aryl migration has been observed in other aryliodonium phenolates and involves an intermediary spiro-Meisenheimer complex.[2a,6] Ethers **6** are new compounds and were fully characterized. Substituent R is found at *para* position, confirming the *ipso* migration of aryl group.



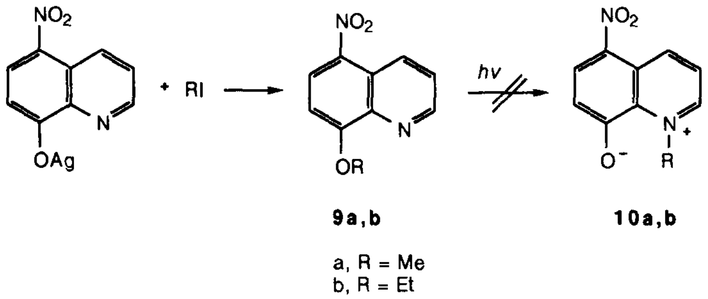
Scheme 2

Solutions of ethers **6** in various solvents have the tendency to obtain a deep purple colour, when they are exposed even to diffused sunlight. Chromatographic separation showed that this intense colour is a result of the formation of aryl-quinolinium-8-olates, **8**. Best results (yields of **8** up to 40-60%) are obtained when benzene solutions of ethers **6** are irradiated with a 250-Watt low pressure Hg lamp for 2 hrs or exposed to direct sunlight for 8-10 hrs. The reaction takes place even in the solid state, as it is indicated by the change of colour, when crystals of **6** are exposed to light.

The only known compound analogous to **8** is methyl-quinolinium-8-olate, prepared from the corresponding methyl iodide salt of oxine.[7] Compounds **8** are crystallized in deep purple needles and their spectroscopic data and elemental analyses are consistent with their structure.[8]

This photochemical aryl migration is most unusual since Kappe and co-workers[9] showed that the photochemical reaction in analogous (but without ring nitrogen) iodo-aryl ethers takes a completely different path: Loss of HI gives rise to dibenzofurans.

The migration of aryl group from **6** to **8** takes place again at the carbon *ipso* to oxygen (R is found at the *para* position in the cases of **8b** and **8c**), indicating the possible intermediacy of a spiro-Meisenheimer complex of type **7**. This assumption is strongly strengthened by the fact that alkyl ethers **9**, prepared by alkylation of the silver salt of 5-nitro-8-hydroxy-quinoline, remained unchanged under irradiation and no alkyl migration to **10** is observed (Scheme 3).



Scheme 3

It must be noted that some attempts to prepare aryl ethers analogous to **9** (with R = Ar) by other arylation methods (Williamson , diaryliodonium salts) have failed. The two step migration of aryl group described provides a facile access to aryl-8-quinolinates, these interesting 1,4 dipoles, the properties of which will be investigated.

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8. Selected spectroscopic data for **8c**. UV-Vis (EtOH): λ_{max} (lg ε) 313 (3.67), 385 (3.60), 495 (3.32) nm; ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.88 (s, 3H), 6.95 (d, 2H, J=9 Hz), 7.17 (d, 2H, J=9 Hz), 7.88 (dd, 1H, J=9 Hz, 7 Hz), 8.37 (d, 1H, J=7 Hz), 9.42 (s, 1H), 10.43 (d,1H, J=9 Hz); MS m/z (rel intensity) 422 (M^+, 40), 392 (10), 249 (41), 206 (56), 178 (100), 151 (39).

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