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Hypervalent Iodine Oxidation of 2-Aryl-1,2,3,4-tetrahydro-4-quinolones: An Easy Access to 2-Aryl-4-quinolones

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HYPERVALENT IODINE OXIDATION OF 2-ARYL-1,2,3,4-TETRAHYDRO-4-QUINOLONES : AN EASY ACCESS TO 2-ARYL-4-QUINOLONES

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Abstract: Oxidation of 2-aryl-1,2,3,4-tetrahydro-4-quinolones (**1a-e**) using iodobenzene diacetate in methanolic potassium hydroxide leads to dehydrogenation of **1** thereby providing an easy access to 2-aryl-4-quinolones (**2a-e**).

It has earlier been shown by us that oxidation of 2'-hydroxychalcones/flavanones with iodobenzene diacetate (IBD) in methanolic potassium hydroxide provides a novel route for the synthesis of cis-3-hydroxyflavanones[1,2]. The formation of these products was established to proceed through the intermediacy of isolable 3-hydroxyflavanone dimethylacetal. In order to extend the scope of this study to nitrogen analogues of flavanones, we investigated the reaction of 2-aryl-1,2,3,4-tetrahydro-4-quinolones (**1a-e**) with IBD under similar conditions.

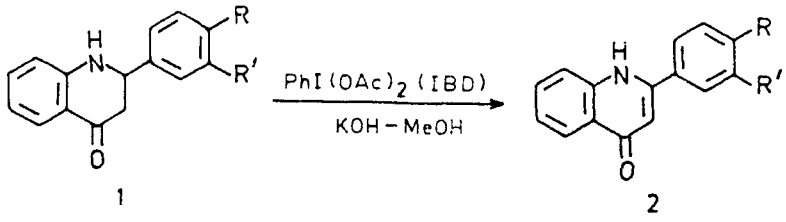
The reaction of 2-phenyl-1,2,3,4-tetrahydro-4-quinolone (**1a**) with IBD under basic conditions (KOH-MeOH) resulted

in the dehydrogenation of **1a** thereby giving 2-phenyl-4-quinolone (**2a**), rather than the expected ∝-hydroxydimethylacetal as observed in the oxidation of flavanones or enolizable ketones[3]. This dehydrogenation route was found to be general, as various substituted 2-aryl-1,2,3,4-tetrahydro-4-quinolones (**1b-e**) yielded corresponding 2-aryl-4-quinolones (**2b-e**) (Scheme I). These quinolone derivatives were identified by the comparison of their mps, IR and ^{1}H NMR spectral data with those reported in literature (Table).

A probable mechanism for the conversion **1** to **2** may involve the formation of intermediate **4** by the electrophilic attack of I(III) reagent, $PhI(OMe)_2$ [from $PhI(OAc)_2$ in KOH-MeOH] at C_3 of enolate **3** generated from **1** with methoxide ions. The intermediate **4** can then lead to the products **2** either by direct elimination process (path a) or via 3-methoxyflavanone **5** (probably <u>cis</u> isomer; path b) (Scheme II).

It must be mentioned that the same intermediate (**4**) could also yield the normal product **6** which are not formed in the present study. The attack of IBD at 'N' atom may also be considered, but less likely as delineated previously[4].

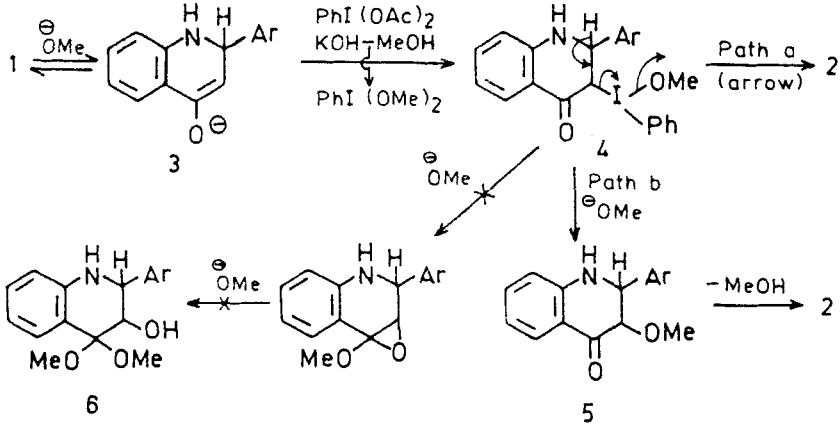
The present hypervalent iodine oxidative approach provides a convenient method for the conversion **1** to **2** which are otherwise available through comparatively difficult routes[5-8].



1 2

1,2; **a,** R = R' = H **d,** R = OMe, R' = H
b, R = Cl, R' = H **e,** R = R' = - OCH_2O-
c, R = Me, R' = H

Scheme I



Scheme II

Experimental

The melting points are uncorrected. IR spectra (nujol) were recorded on Perkin Elmer IR-842 spectrophotometer, ^1H NMR spectra (TFA) on Perkin Elmer R-32 machine using TMS as internal standard. The 2-aryl-1,2,3,4-tetrahydro-4-

Table : 2-Aryl-4-quinolones prepared according to Scheme I.

Product	Yield[a] (%)	mp(Lit mp)[5,6] (°C)
2a	85	251-53 (253-54)
2b	89	254-55 (254-55)
2c	80	291-93 (294-96)
2d	75	294-96 (294-96)
2e	78	247-48 (246-48)

[a] yields are based on isolated crystalline product with respect to **1** used.

quinolones were obtained from 2'-aminoacetophenone according to the literature procedure[9,10].

Preparation of 2-aryl-4-quinolones (2a-e)

General Procedure : To a solution of 2-aryl-1,2,3,4-tetrahydro-4-quinolone (**1a-e**, 1 mmol) in methanol (20 ml) was added a solution of potassium hydroxide (3 mmol) in methanol (20 ml) and stirred for 10 min. Iodobenzene diacetate (1.1 mmol) was subsequently added in portions and the resulting mixture was allowed to stir for 12-18 hr at 60°C. Excess methanol was removed under vacuo and the contents were poured in cold dilute HCl (ca. amount). The product separated out was filterted, treated with aq. $NaHCO_3$ and crystallised from methanol or passed through a column of silica gel to afford 2-aryl-4-quinolones (**2a-e**).

Acknowledgement

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