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First Report of the Isolation of Novel Oxiranes in the I(III) Mediated Oxidation of 1-(4-Nitrophenyl)-3-arylprop-2-en-1-ones

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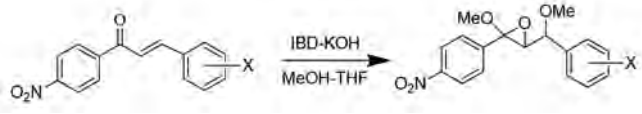
ABSTRACT The study offers first example of the isolation of novel oxiranes, 2-methoxy-3-(methoxy(aryl)methyl)-2-(4-nitrophenyl)oxiranes in the iodobenzene diacetate mediated oxidation of 1-(4-nitrophenyl)-3-arylprop-2-en-1-ones which have earlier been proposed as intermediates in such oxidation reactions.

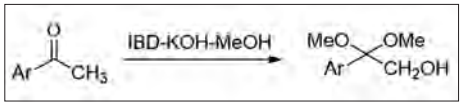


KEYWORDS Acetals, Diarylchalcones, Iodobenzene diacetate, Oxiranes.

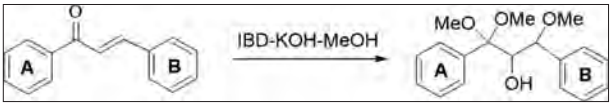
The organohypervalent iodine (III) reagent with two heteroatom ligands, iodobenzene diacetate, $PhI(OAc)_2$ (IBD), has been employed for the oxidations of wide applicability. This organometallic reagent has found synthetic utility in α-functionalization of carbonyl compounds, carbon-carbon bond formation, rearrangements, cyclizations, etc.[1-3] A particularly useful methodology for the oxidative α-functionalization of enolizable carbonyl compounds involves IBD in methanolic potassium hydroxide.[4-6]

The reaction is quite general and results in the synthesis of α-hydroxydimethylacetals (**Scheme 1**). The reaction is also applicable to α,β-unsaturated carbonyl compounds which cannot form anion by α-hydrogen abstraction such as chalcone, chromone, flavone and flavanone to give α-hydroxy-β-methoxy dimethyl acetal products regiospecifically as well as stereospecifically (**Scheme 2**).[7-11]

In the class of diarylchalcones, the reaction has been applied only on the parent enone, i.e., diphenylprop-2-en-1-one. Till now, there is no report on the IBD mediated oxidation of the chalcone derivatives, possessing different substituents on aromatic rings **A** and **B**. To extend the scope of the reaction, we started the project on the differently substituted chalcones. The purpose was to synthesize several new dimethyl acetals which are themselves important entities in organic chemistry and can prove to be significant precursors for the synthesis of α-hydroxyketones. With this objective, the reaction was carried on the diarylchalcones substituted on the rings **A** and **B** at once or separately. In the course of the study, many of the substituted chalcones



Scheme 1



Scheme 2

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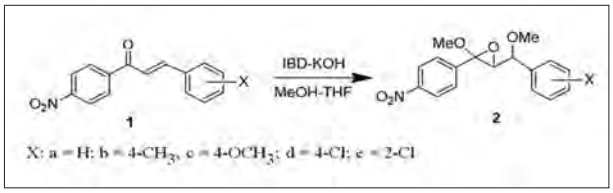

Scheme 3

produced the similar results (acetal products) as the reported one. However, the results were quite different with the chalcones having nitro substituent on the *para* position of the ring **A**. In this case, the reaction did not follow the reported trend. The present communication is an effort to report the preliminary findings of the IBD mediated reaction of 1-(4-nitrophenyl)-3-arylprop-2-en-1-one.

Initially, the reaction was carried out with the chalcone, 1-(4-nitrophenyl)-3-phenylprop-2-en-1-one (**1a**), containing 4-NO_2 substituent on ring **A** and unsubstituted ring **B**. The formation of a single product, different from the expected acetal was observed in the reaction. The 1H nuclear magnetic resonance spectrum of the product showed the presence of two methoxy groups instead of three in the case of acetals. The high-resolution mass spectrometry (HRMS) showed a peak at M-29 which is characteristic of epoxides and is formed due to 1,2-aryl shift followed by the loss of formyl radical. The product was fully analyzed and was confirmed to be an oxirane, 2-methoxy-3-(methoxy(phenyl)methyl)-2-(4-nitrophenyl)oxirane **2a**.[12] Further, the reaction was carried out with the enones substituted at ring B (with electron releasing and withdrawing groups) along with 4-NO_2 substituent at ring A (**1b-e**). The corresponding oxirane products **2b-e** were obtained in all the cases (**Scheme 3**).

Therefore, it can be inferred from the results, that formation of the product, acetal or epoxide, in the reaction depended only on the substituent on ring A of the reactant, irrespective of either the ring B is substituted (with *ortho* or *para* substituent) or unsubstituted. It is relevant to mention here that the originally proposed mechanism of the reaction refers the existence of such an epoxide. Thus, the results of this study provide strong support for the validity of the proposed mechanistic pathway.

CONCLUSION

The reaction offers an efficient route for the synthesis of novel oxiranes from the chalcones having *para* nitro group on ring A. The experiments pertaining to explore the full scope of the reaction by taking differently substituted rings (A and B) and the conversion of epoxides to the corresponding acetals are going on. The results along with the application of the reaction to hetaryl chalcones will be published later on as full report.

ACKNOWLEDGMENT

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[12] Two-methoxy-3-(methoxy(phenyl)methyl)-2-(4-nitrophenyl)oxirane (2a). Mp 80-81 ºC, yield 52%. IR (KBr, cm-1): No peak in the CO region. 1H NMR ($CDCl_3$, 300 MHz, δ): 2.99 (d, 1H, J = 7.8 Hz, C3-H), 3.33, 3.37 (s, 3H, OCH_3), 4.35 (d, 1H, J = 7.8 Hz, CH-OCH_3), 7.32-7.36 (m, 5H, ArH), 7.54-7.56 (m, 2H, ArH), 8.16-8.19 (m, 2H, ArH); HRMS: Calcd. for C16H16NO4: 286.1079 (M+-29) Found: 286.0257.

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