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Organoiodine (III) mediated oxidation of enones in methanolic potassium hydroxide

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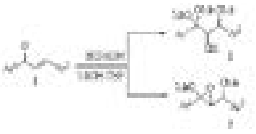
Background: The hypervalent iodine (III) compounds, (diacetoxyiodo)benzene (DIB) possess numerous applications as oxidizing reagent. A particularly useful methodology for the oxidative α-functionalization of enolizable carbonyl compounds involves DIB in methanolic potassium hydroxide resulting in the synthesis of α-hydroxydimethylacetals. The reaction is also applicable to enones which cannot form anion by α-hydrogen abstraction such as chromone, chalcone, flavones and flavanone.

Aim: To explore the fate of the reaction on the different chalcone derivatives to ascertain the substituent effect.

Methodology: Initially, the reaction was applied to the chalcones having different substituents on ring 1, keeping the ring 2 unsubstituted. The oxidation reaction, indeed, afforded the expected acetals in all the cases except with the chalcone possessing *p*-NO_2 substituent on ring 1. Formation of 2-methoxy-3-(methoxy(phenyl)methyl)-2-(4-nitrophenyl)oxirane was observed in this case. Next, the reaction was carried out with the chalcones differently substituted at ring 2 to determine the effect of the ring 2 substituents on the oxidative I(III) mediated approach. Interestingly, the corresponding acetal products were obtained in all the cases. To extend further the scope of the oxidative transformation, the reaction was performed with the chalcones substituted on both the rings (1 and 2).

Findings: An interesting fact came forth that when the substituent is *p*-NO_2 on ring 1 of the reactant, the product was always the oxirane, irrespective of either the ring 2 is substituted (with *ortho* or *para* substituent) or unsubstituted.

Conclusion & Significance: The results show the wider applicability of the I(III) mediated methodology for the oxidation of α,β-unsaturated carbonyl compounds. The reaction offers an efficient route for the synthesis of novel oxiranes.



Recent publications

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2. Pundeer R and Vijaykiran (2016) Organoiodine(III) mediated one-pot synthesis of several new coumarinyl-triazolo-triazines. Organic Chemistry: An Indian Journal 12:106.
3. Pundeer R and Vijaykiran (2016) Green and expeditious synthesis of some 2-amino/arylamino-4-(1-naphthyl)thiazole derivatives using [hydroxyl(tosyloxy)iodo]benzene. Indian Journal of Heterocyclic Chemistry 25:311-17.
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Biography

Rashmi Pundeer is mainly concerned with the development of simple synthetic strategies for widely used organic compounds through the intermediacy of versatile, ecofriendly and readily available oxidizing reagents, the hypervalent iodine(III) reagents particularly, (diacetoxyiodo)benzene (DIB), [hydroxyl(tosyloxy)iodo] benzene (HTIB) and (dichloroiodo)benzene. She is also working towards the synthesis of nitrogen containing heterocyclic compounds particularly five and six membered ones of potential medicinal interest. Three scholars have completed Doctorate degree under her supervision.

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