



Original article

A convenient catalytic oxidative 1,2-shift of arylalkenes for preparation of α -aryl ketones mediated by NaIMin Zhu^{a,*}, Yang Zhao^b^a College of Biological and Environmental Sciences, Zhejiang Shuren University, Hangzhou 310015, China^b Foreign Language School, Zhejiang Shuren University, Hangzhou 310015, China

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ABSTRACT

Using a catalytic amount of NaI and a stoichiometric oxidant Oxone[®], a convenient procedure has been developed for the catalytic oxidative 1,2-shift of arylalkenes in CH₃CN/H₂O at room temperature, which provides the corresponding α -aryl ketones in moderate to good yields. In this protocol, sodium iodide is first oxidized into hypoiodous acid, which reacts with arylalkene to afford iodohydrin. Then, the iodohydrin is transformed into the α -aryl ketone via an oxidative 1,2-shift rearrangement.

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1. Introduction

Hypervalent iodine reagents have found broad application in organic chemistry and nowadays frequently used in synthesis as they are nonmetallic oxidation reagents and avoid the issues of toxicity of many transition metals commonly involved in such processes [1–10]. Using the hypervalent iodine reagent, [hydroxyl(tosyloxy)]iodobenzene (Koser's reagent, HTIB), Koser and co-workers have developed a convenient oxidative 1,2-shift procedure of arylalkenes, with which the corresponding α -aryl ketones have been obtained in good yields [11–13]. In recent years, the catalytic utilization of hypervalent iodine reagents is increasing in importance, with the growing interest in the development of environmentally benign synthetic transformations [14–18]. In these reactions, a catalytic amount of an iodine-containing molecule together with a stoichiometric oxidant is used. The oxidant generates the hypervalent iodine reagent *in situ*, and after the oxidative transformation, the reduced iodine-containing molecule is re-oxidized. Very recently, Purohit and co-workers just reported the first catalytic oxidative 1,2-shift of arylalkenes by the *in situ* generated hypervalent iodine species [19]. However, the reaction conditions are somewhat complex and the yields are not as high as those Koser's group reported [13]; moreover, the

unusual 2-iodo-5-methylbenzenesulfonic acid is used as catalyst in the method. Therefore, the simple and convenient catalytic oxidative 1,2-shift reactions are still desired.

Due to that iodobenzene (PhI) can be prepared by the reaction of molecule iodine (I₂) with benzene in the presence of oxidants, Togo and co-workers have developed a new way for the α -tosyloxylation of ketones using I₂ as catalyst in place of the expensive PhI, which has been demonstrated via hypervalent iodine intermediate [20]. At the same time, we have also investigated the possibility of using inorganic iodides which are more environmentally benign in place of PhI in the catalytic reaction, and a convenient route for monobromination of electron-rich aromatic compounds using I₂ or NH₄I as catalyst has been developed [21]. Herein, we wish to report a novel and convenient catalytic oxidative 1,2-shift rearrangement of arylalkenes using a catalytic amount of NaI together with a stoichiometric Oxone[®] (2KHSO₅·KHSO₄·K₂SO₄) as the terminal oxidant, and to the best of our knowledge this method has not been reported before.

2. Experimental

A typical procedure for the catalytic oxidative 1,2-shift of arylalkenes: To a mixture solvent MeCN–H₂O (5:1) (2 mL), α -methylstyrene (0.5 mmol), Oxone[®] (1.0 mmol) and NaI (0.05 mmol) were added. The mixture was stirred at room temperature for 15 h, then H₂O (5 mL) was added. Extraction of the mixture with CH₂Cl₂ (3 × 5 mL) and the combined organic

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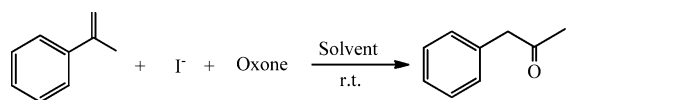
layer was dried over anhydrous Na_2SO_4 , filtered, and concentrated under reduced pressure. The residue was purified on silica gel plate (5:1 hexane-ethyl acetate) to give 1-phenylpropan-2-one in 81% of yield. Colorless oil; ^1H NMR (500 MHz, CDCl_3): δ 7.39–7.36 (m, 2H), 7.31–7.28 (m, 1H), 7.22 (d, 2H, $J = 8.4$ Hz), 3.71 (s, 2H), 2.17 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3): δ 206.5, 134.3, 129.3, 128.8, 127.1, 51.1, 29.2; IR (film, cm^{-1}): ν 1713; MS (EI, m/z , %): 134 (M^+ , 100).

3. Results and discussion

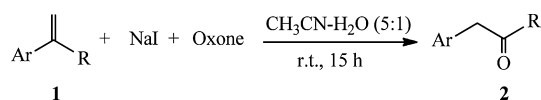
We first examined the reaction of α -methylstyrene with 1.5 equiv. of oxidant Oxone[®] in the presence of 0.1 equiv. of NH_4I in water at room temperature, and found that the desired product 1-phenylpropan-2-one was obtained in only 5% yield after 20 h (Table 1, entry 1). When several mixture solvents were used in place of water, the reaction gave the product in great different yields, in which the mixture solvent MeCN- H_2O (5:1) was proved to be the favorable solvent system for the reaction (entries 2–10). Compared with NH_4I , KI and NaI were more active in the reaction, in which NaI was the most effective one, and 0.1 equiv. of it was the best choice (entries 2, 11–14). However, if NaI was absent, no desired product was observed (entry 15). The amount of Oxone[®] was checked and 2.0 equiv. of it was suitable for the reaction (entries 12, 16–18). The suitable reaction time should be 15 h (entries 16, 19–21).

Under the optimum reaction conditions, we investigated the catalytic oxidative 1,2-shift reaction of 1.0 equiv. of arylalkenes (1), 2.0 equiv. Oxone[®] and 0.1 equiv. of NaI in $\text{CH}_3\text{CN}-\text{H}_2\text{O}$ (5:1) at room temperature for 15 h (Scheme 1), the results are summarized in Table 2.

Table 1
Optimization of the catalytic oxidative 1,2-shift of α -methylstyrene

					
Entry	Oxone (equiv.)	I^- (equiv.)	Solvent	Time (h)	Yield (%) ^a
1	1.5	NH_4I (0.1)	H_2O	20	5
2	1.5	NH_4I (0.1)	MeCN- H_2O (5:1)	20	71
3	1.5	NH_4I (0.1)	$\text{CH}_2\text{Cl}_2-\text{H}_2\text{O}$ (5:1)	20	13
4	1.5	NH_4I (0.1)	THF- H_2O (5:1)	20	4
5	1.5	NH_4I (0.1)	$\text{CH}_3\text{OH}-\text{H}_2\text{O}$ (5:1)	20	65
6	1.5	NH_4I (0.1)	$\text{CF}_3\text{CH}_2\text{OH}-\text{H}_2\text{O}$ (5:1)	20	68
7	1.5	NH_4I (0.1)	EtOAc- H_2O (5:1)	20	18
8	1.5	NH_4I (0.1)	MeCN- H_2O (1:1)	20	19
9	1.5	NH_4I (0.1)	MeCN- H_2O (2:1)	20	35
10	1.5	NH_4I (0.1)	MeCN- H_2O (10:1)	20	63
11	1.5	KI (0.1)	MeCN- H_2O (5:1)	20	74
12	1.5	NaI (0.1)	MeCN- H_2O (5:1)	20	76
13	1.5	NaI (0.2)	MeCN- H_2O (5:1)	20	78
14	1.5	NaI (0.05)	MeCN- H_2O (5:1)	20	57
15	1.5	–	MeCN- H_2O (5:1)	20	0
16	2.0	NaI (0.1)	MeCN- H_2O (5:1)	20	82
17	1.2	NaI (0.1)	MeCN- H_2O (5:1)	20	63
18	1.0	NaI (0.1)	MeCN- H_2O (5:1)	20	55
19	2.0	NaI (0.1)	MeCN- H_2O (5:1)	10	65
20	2.0	NaI (0.1)	MeCN- H_2O (5:1)	15	81
21	2.0	NaI (0.1)	MeCN- H_2O (5:1)	24	80

^a Isolated yield.



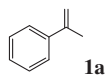
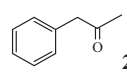
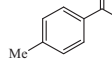
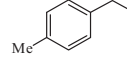
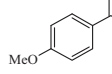
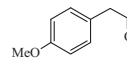
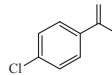
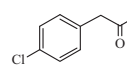
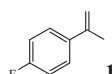
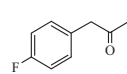
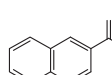
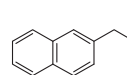
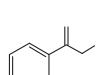
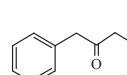
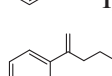
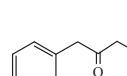
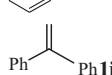
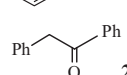
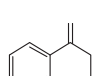
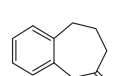
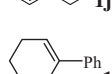
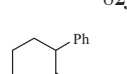
Scheme 1. The catalytic oxidative 1,2-shift of arylalkenes.

As shown from Table 2 that the reaction was compatible with most of the studied arylalkenes and the corresponding α -aryl ketones were obtained in moderate to good yields (entries 1–11). It was notable that the arylalkenes with electron-donating groups on the benzene ring usually led to better yields than those having electron-withdrawing groups on benzene ring (entries 2–5). Due to that the hinder effect of groups, arylalkenes **1g**, **1h** and **1i** resulted in the corresponding α -aryl ketones with the somewhat lower yields compared with **1a** (entries 1, 7–9). 1-Phenyl cyclohexene (**1k**), a trisubstituted alkene, when it was treated under the same conditions, the respect product **2k** was afforded in 70% yield (entry 11).

According to the above results, a plausible reaction pathway is shown in Scheme 2. Thus, NaI is first oxidized to HOI by Oxone[®], which reacts with α -methylstyrene in the presence of water to form an iodohydrin. The iodohydrin is then easily transformed into the highly unstable hypervalent iodine iodosyl intermediate by the continuing oxidation of Oxone[®] [1,2], which rearranges via a 1,2-shift procedure to afford the final product 1-phenylpropan-2-one.

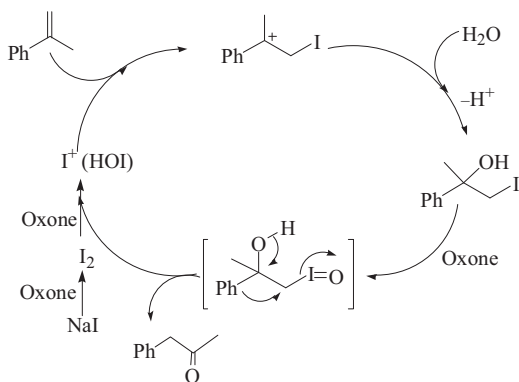
To identify it, α -methylstyrene was first treated with HOI [22], which provided iodohydrin in good yield. Then, the reaction of iodohydrin with Oxone[®] was examined. The result showed that in the absence of Oxone[®], the desired product 1-phenylpropan-2-one was not observed after a long reaction time. However, when

Table 2
The result of the catalytic oxidative 1,2-shift of arylalkenes.

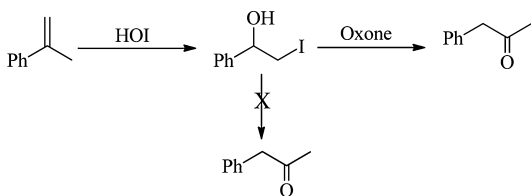
Entry	Substrate (1)	Product (2)	Yield (%) ^a
1			81
2			83
3			85
4			67
5			55 ^b
6			76
7			72
8			70
9			65
10			62
11			70

^a Isolated yield.

^b Reaction time was 24 h.



Scheme 2. Proposed mechanism for the catalytic oxidative 1,2-shift of arylalkenes.



Scheme 3. Identification of the above mechanism.

Oxone[®] was added to the reaction mixture, the desired product was obtained in good yield. Therefore, the *in situ* generated hypervalent iodine intermediate was responsible for the reaction (Scheme 3).

4. Conclusion

We have developed a new and convenient strategy for the catalytic oxidative 1,2-shift reaction of arylalkenes mediated by NaI together with Oxone[®] in MeCN-H₂O (5:1) at room temperature. The method using a catalytic amount of inorganic iodide replacement of expensive aryl iodides has some advantages such as mild reaction conditions, simple procedure and more environmentally benign. Moreover, it extends the scope of hypervalent iodine reagents in organic synthesis.

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