

Highly efficient RuCl₃-catalyzed disproportionation of (diacetoxyiodo)benzene to iodylbenzene and iodobenzene; leading to the efficient oxidation of alcohols to carbonyl compounds

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Abstract—(Diacetoxyiodo)benzene (DIB) selectively oxidizes primary and secondary alcohols to the respective carbonyl compounds in the presence of RuCl₃ (0.8–1.0 mol %) at room temperature in aqueous acetonitrile. This reaction proceeds via an initial instantaneous Ru-catalyzed disproportionation of DIB to iodobenzene and iodylbenzene with the latter acting as the actual stoichiometric oxidant toward alcohols.

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During the past decade hypervalent iodine compounds have attracted a significant interest as mild, selective and environmentally benign reagents in synthetic organic chemistry.¹ It has also been found that transition metals have a dramatic catalytic effect on some oxidations with hypervalent iodine reagents.^{1–4} In particular, iodosylbenzene is widely used as an oxidant in the transition metal catalyzed epoxidation of alkenes and hydroxylation of hydrocarbons.¹ Likewise, (diacetoxyiodo)arenes are efficient oxidizers in the Pd(OAc)₂-catalyzed selective acetoxylation of arene and alkene C–H bonds.² The catalytic effect of transition metals on the synthetically important reaction of oxidation of alcohols by hypervalent iodine reagents has been less investigated.^{3,4} It has been demonstrated that benzylic and allylic alcohols can be oxidized by iodosylbenzene to the corresponding carbonyl compounds in the presence of (salen)Cr(III) complex (15 mol %) and 4-phenylpyridine *N*-oxide (30 mol %).³ Mueller and Godoy reported in 1981 that several complexes of ruthenium can catalyze the oxidation of alcohols to carbonyl compounds

and carboxylic acids using excess iodosylbenzene as the oxidizer in dichloromethane solution at room temperature.⁴ In the present letter we want to report a simple and highly efficient RuCl₃-catalyzed selective oxidation of alcohols to carbonyl compounds by (diacetoxyiodo)benzene (DIB). We have also received experimental evidence that this reaction proceeds via an initial instantaneous Ru-catalyzed disproportionation of DIB to iodobenzene and iodylbenzene with the latter acting as the actual stoichiometric oxidant toward alcohols.

We have found that the addition of RuCl₃ (0.8–1.0 mol %) to the solution of equimolar amounts of (diacetoxyiodo)benzene and an alcohol at room temperature in aqueous acetonitrile results in an instantaneous interaction with the formation of a precipitate which then slowly completely dissolves after stirring for 0.5–24 h (reaction time varies for specific alcohols). NMR spectra of the reaction mixtures indicated in each case an almost quantitative conversion of alcohol to the respective carbonyl compound. The aldehydes and ketones (**2**) formed from the oxidation of each alcohol (**1**) were further converted to the 2,4-dinitrophenylhydrazone derivatives (**3**) and identified by comparison of their melting points with the ones reported in the literature data (Scheme

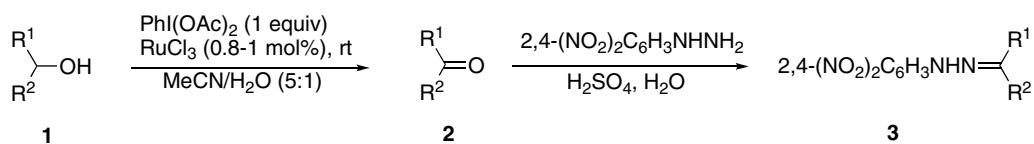
Keywords: Hypervalent iodine; (Diacetoxyiodo)benzene; Iodylbenzene; Oxidation; Catalysis.

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1).⁵ The preparative yields and melting points of 2,4-dinitrophenylhydrazones **3** obtained from alcohols **1** are summarized in Table 1.

To clarify the nature of the actual oxidizing species in this reaction, we have isolated and identified the micro-

crystalline precipitate that forms immediately after addition of RuCl₃ to the solution of (diacetoxyiodo)benzene and an alcohol in aqueous acetonitrile. Based on the NMR data and melting point (229 °C, expl), this initial product was identified as iodylbenzene, PhIO₂. Further investigation has revealed that alcohol (**1**) is not



Scheme 1.

Table 1. RuCl₃-catalyzed oxidation of alcohols to carbonyl compounds by (diacetoxyiodo)benzene

Entry	Alcohol 1	Time (h)	Yield of 3 ^a (%)	Mp of 3 (lit. mp) (°C)	Ref.
1	(+)-Menthol	2.0	92	146–148 (145)	6
2	3-Phenyl-1-propanol	0.5	94	156–157 (152–153)	7
3	1-Octanol	1.5	71	100–102 (100–101.5)	7
4		1.5	96	256–258 (256.5–257.5)	8
5	PhCH ₂ OH	1.0	95	241–242 (239–240)	9
6		1.5	79 ^b	Oil	— ^c
7		1.5	90	147–148 (146–147)	10
8		2.5	93	157–159 (157–162)	7
9		5.0	73	259–261 (258.5–259.5)	11
10		1.5	88	239–241 (242)	12
11		0.5	82	256–257 (258–259)	7
12		9.3	70 ^d	292–293 (293–294)	9
13		6.0	37 ^c	146–148 (148–150)	13
14		24	62 ^d	168–170 (164–166)	14

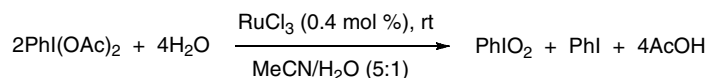
^a Isolated yields of 2,4-dinitrophenylhydrazones.

^b Yield of aldehyde (**2**) measured by GC.

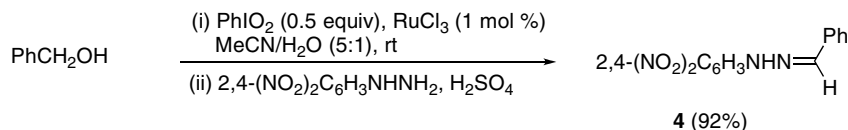
^c Aldehyde was identified by MS (M⁺ = 140.12).

^d About 20% of unreacted alcohol present according to ¹H NMR.

^e Formation of black tar was observed in this reaction.



Scheme 2.



Scheme 3.

involved in the initial step of this reaction. The addition of a catalytic RuCl_3 (0.4 mol %) to a solution of (diacetoxyiodo)benzene in aqueous acetonitrile at room temperature results in an instantaneous quantitative disproportionation of DIB to a 1:1 mixture of iodobenzene and iodylbenzene according to NMR data (Scheme 2). This unique and highly efficient disproportionation can be conveniently performed in a preparatory scale affording analytically pure PhIO_2 in a moderate isolated yield.¹⁵

When this reaction is performed in the presence of an alcohol, the initially formed iodylbenzene further acts as the stoichiometric oxidant slowly converting alcohol to the carbonyl compound. In a special experiment, benzyl alcohol was oxidized with PhIO_2 (0.5 equiv) in the presence of RuCl_3 (1 mol %) under conditions identical to the reaction of (diacetoxyiodo)benzene (Table 1, entry 5). The reaction (Scheme 3) was complete in 40 min affording the expected 2,4-dinitrophenylhydrazone **4** in a 92% isolated yield.¹⁶ This example (Scheme 3) illustrates that PhIO_2 can serve as an efficient oxidizer in the Ru-catalyzed oxidations of alcohols. In practical use, however, the readily available and safe (diacetoxyiodo)benzene is a more convenient oxidizer compared to the explosive and unavailable from commercial sources iodylbenzene.

It is known from the literature that RuCl_3 as well as other ruthenium salts and complexes can catalyze the oxidation of alcohols with various stoichiometric oxidants.¹⁷ For example, the H_2O_2 – RuCl_3 system can non-selectively oxidize alcohols to carbonyl compounds and carboxylic acids at 80 °C.¹⁸ It has been proposed in particular that the oxo ruthenium complexes of a lower oxidation state are involved as the active intermediates in these catalytic cycles.¹⁸ We assume that the similar intermediate oxo ruthenium complexes are responsible for the oxygen transfer steps in the mechanisms of disproportionation of iodine(III) species and oxidation of alcohols.

In conclusion, we have found a simple and highly efficient procedure of RuCl_3 -catalyzed selective oxidation of alcohols to carbonyl compounds using (diacetoxyiodo)benzene. We have also received experimental evidence that this reaction proceeds via an initial instantaneous Ru-catalyzed disproportionation of (diacetoxyiodo)benzene to iodobenzene and iodylbenzene with the

latter acting as the actual stoichiometric oxidant toward alcohols.

Acknowledgments

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15. *Experimental procedure for RuCl₃-catalyzed disproportionation of (diacetoxyiodo)benzene*: To a solution of (diacetoxyiodo)benzene (161 mg, 0.5 mmol) in 1 mL of aqueous acetonitrile (MeCN–H₂O, 5:1) an aqueous solution of RuCl₃ (4 μL of 0.5 M solution; 0.002 mmol) was added via a syringe under stirring at room temperature. An immediate formation of a white microcrystalline precipitate of PhIO₂ was observed. After additional stirring for 5 min, the precipitate was filtered, washed with cold aqueous acetonitrile (MeCN–H₂O, 5:1), and dried to afford 36 mg (61%) of iodylbenzene, mp 229–230 °C (expl), IR (KBr): 731, 713 (IO₂); ¹⁹F NMR (DMSO-*d*₆) δ 7.92 (m, 2H) 7.59 (m, 3H); ¹³C NMR (DMSO-*d*₆) δ 150.8 (C-IO₂), 131.7, 129.1, 126.6.
16. *RuCl₃-catalyzed oxidation of benzyl alcohol with iodylbenzene*: To a mixture of benzyl alcohol (108 mg, 1 mmol) and iodylbenzene (161 mg, 0.5 mmol) in 1 mL of aqueous acetonitrile (MeCN–H₂O, 5:1) an aqueous solution of RuCl₃ (10 μL of 0.5 M solution; 0.005 mmol) was added under stirring at room temperature. The reaction mixture was stirred for 40 min until the complete dissolution of iodylbenzene and then 9 mL of a standard solution of 2,4-dinitrophenylhydrazine was added. The precipitate was filtered, washed with water, and dried to afford 263 mg (92%) of 1-benzylidene-2-(2,4-dinitrophenyl)hydrazine **4**, mp 241–242 °C (lit.⁹ 239–240 °C).
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