An Efficient Catalytic Sulfonyloxylactonization of Alkenoic Acids Using Hypervalent Iodine(III) Reagent

Jie Yan,* Hong Wang, Zhenping Yang, Yan He

College of Chemical Engineering and Materials Sciences, Zhejiang University of Technology, Hangzhou 310032, Zhejiang, P. R. of China Fax +86(571)88320238; E-mail: jieyan87@zjut.edu.cn

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Abstract: A novel and efficient catalytic method for sulfonyloxylactonization of alkenoic acids is reported. (Diacetoxyiodo)benzene could be used as a recyclable catalyst in combination with *m*-chloroperbenzoic acid as an oxidant in the presence of sulfonic acid to effect the cyclization of various alkenoic acids in CH₂Cl₂ at room temperature, giving sulfonyloxylactones in good yields.

Key words: sulfonyloxylactonization, hypervalent iodine reagent, catalytic cyclization

Organic hypervalent iodine reagents have found broad application in organic chemistry and frequently used in synthesis due to their chemical properties and reactivity similarities to those of Hg(II), Tl(III), and Pb(IV), but without the toxic and environmental problems of these heavy-metal congeners.¹ They are usually used as mild oxidants,² and also as electrophilic reagents, with them various cyclizations of unsaturated systems have been carried out.³ Koser and co-workers first reported the tosyloxylactonization of alkenoic acids with the hypervalent iodine reagent, [hydroxy(tosyloxy)iodo]benzene (HTIB, Koser's reagent), and the ability of HTIB to introduce the tosylate ligand into alkenoic acids received much attention.^{3b} Recently, the catalytic utilization of hypervalent iodine reagents is increasing in importance, with growing interest in the development of environmentally benign synthetic transformations.⁴ Kita and co-workers used catalytic amounts of hypervalent iodine(III) reagents and meta-chloroperbenzoic acid (MCPBA) as an oxidant in the spirocyclization of phenol and amide derivatives.⁵ Ochiai and co-workers reported the a-acetoxylation of ketones with the combination of a catalytic amount of an aryl iodide and MCPBA as the oxidant.⁶ In these catalytic reactions, a catalytic amount of an iodine-containing molecule together with a stoichiometric oxidant were used. The oxidant generated the hypervalent iodine reagent in situ, and after the oxidative transformation, the reduced iodine-containing molecule was re-oxidized. PhI-catalyzed α -tosyloxylation of ketones with MCPBA and ptosylic acid (TsOH) has also received considerable attention.⁷ However, the catalytic sulfonyloxylactonization of alkenoic acids has not been reported before.

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In order to extend the scope of catalytic use of organoiodines(III) for organic synthesis, we have investigated a series of cyclizations of alkenoic acids using catalytic amounts of hypervalent iodine(III) reagents and MCPBA as a stoichiometric chemical oxidant. Herein, we wish to report the first example of the catalytic sulfonyloxylactonization of alkenoic acids.

Initially, we examined the tosyloxylactonization of 4-pentenoic acid (1a) with 0.1 equivalents of (diacetoxyiodo)benzene (DIB) in the presence of the equal equivalent of TsOH (2a) and MCPBA in CH_2Cl_2 at room temperature. The reaction proceeded smoothly and gave

Table 1Optimization of the Tosyloxylactonization of 4-PentenoicAcid



	i a	20			Ja	
Entry	DIB (equiv)	MCPBA (equiv)	TsOH (equiv) ^a	Solvent	Time (h)	Yield (%) ^b
1	0.1	1	1	CH ₂ Cl ₂	1	45
2	0.1	1	1	CH_2Cl_2	2	53
3	0.1	1	1	CH_2Cl_2	4	69
4	0.1	1	1	CH_2Cl_2	8	72
5	0.1	1	1	CH_2Cl_2	16	75
6	0.1	1	1	CH_2Cl_2	24	82
7	0.1	1	1	CH ₂ Cl ₂	92	84
8	0.1	2	2	CH ₂ Cl ₂	24	84
9	0.05	1	1	CH_2Cl_2	24	63
10	0.02	1	1	CH_2Cl_2	24	51
11	0.1	1	1	MeCN	24	62
12	0.1	1	1	MeCN	24	50
13	0.1	1	1	THF	24	54
14	0.1 ^c	1	1	CH_2Cl_2	24	81
15	0	1	1	CH_2Cl_2	24	0

^a Ts, 4-MeC₆H₄SO₂.

^b Isolate yields.

^c PhI was used instead of DIB.

the desired product of 5-tosyloxy-4-pentanolactone (**3a**) in 45% yield in 1 hour (Table 1, entry 1). Then, the reaction conditions were optimized. As the reaction time was prolonged, the yield of **3a** was increased (entries 1–7) and 24 hours was the best suitable reaction time. The amount of catalyst DIB was influential (entries 9 and 10), and 0.1 equivalent was the best choice. As a suitable solvent, CH_2Cl_2 was the most preferred (entries 6, 11–13). When PhI was used instead of DIB, nearly the same result was obtained (entry 14). In the absence of DIB, the sulfony-loxylactonization was not observed (entry 15). Other co-oxidants such as sodium perborate and Oxone[®] [c1] were also not successful.

Under the optimized reaction conditions, we investigated the catalytic sulfonylactonization of equal equivalent alkenoic acids **1**, TsOH **2a** or (+)-10-camphorsulfonic acid (**2b**) and MCPBA with 0.1 equivalents DIB (Scheme 1), and the results are summarized in Table 2.⁸ It was found that good yields of 5-sulfonyloxy-4-pentanolactones were obtained for a series of 4-pentenoic acids (entries 1–3, 7– 10). Similar treatment of 5-hexenoic acid provided 6-sulfonyloxy-5-hexanolactones in moderate yields (entries 4 and 11). When 3-butenoic acid and *trans*-3-hexenoic acids were treated with 2a under the same reaction conditions, only the unsaturated lactones were given (entries 5 and 6), but not the desired sulfonylactons. It was revealed by ¹H NMR spectroscopy that the desired 3-sulfonyloxy-4-butanolactones were first formed, but then further transformed into the unsaturated lactones during workup procedure.



Scheme 1 Hypervalent iodine(III) catalyzed sulfonylactonization of alkenoic acids

Table 2 Hypervalent Iodine(III) Catalyzed Sulfonylactonization of Alkenoic Acids

Entry	Alkenoic acid 1	Sulfonic acid 2	Sulfonyloxylactone 3 ^a	Yield (%) ^b
1	H ₂ C=CH(CH ₂) ₂ CO ₂ H 1a	TsOH 2a		82
2	он Ib	2a		83
3	OH Ic	2a		83
4	$H_2C=CH(CH_2)_3CO_2H$ 1d	2a	O O O O O TS	52
5	H ₂ C=CHCH ₂ CO ₂ H 1e	2a	3d	45
6	OH If	2a		30
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Entry	Alkenoic acid 1	Sulfonic acid 2	Sulfonyloxylactone 3 ^a	Yield (%) ^b
7	1a	(+)-10-camphorsulfonic acid 2b	OCS	83
8	1b	2b	3g	76
9	1c	2b	3h	75
10	Ig	2b		87
11	1d	2b	$3_{\rm J}$	57

Table 2 Hypervalent Iodine(III) Catalyzed Sulfonylactonization of Alkenoic Acids (continued)

^a Ts, 4-MeC₆H₄SO₂; Cs, (+)-10-camphorylsulfonyl. ^b Isolated yield.

In 1988, Koser and co-workers reported another lactonizaton using the hypervalent iodine reagent, {hydroxy[(bis(phenyloxy)phosphoryl)oxy]iodo}benzene, and they found when 2-methyl-4-pentenoic acid (1b) was treated with the hypervalent iodine reagent, the products were a mixture of diastereomers, with a ratio varied from 1.2 to 1.4:1.3^c In our reaction protocol, we also found when 1b was used the corresponding 5-sulfonyloxy-4pentanolactones were obtained as a mixture of diastereomers, with a ratio varied from 2.7:1 for p-tosylic acid to 2.4:1 for camphorsulfonic acid, respectively, as determined by examination of the ¹H NMR spectra of sulfonylactones. When 3-methyl-4-pentenoic acid (1c) was reacted under the same conditions, the ratios of the mixture of diastereomers were 1.7:1 and 2.0:1 for p-tosylic acid and camphorsulfonic acid, respectively, which were somewhat lower as compared to compound 1b.

A proposed mechanism for the catalytic cycle of sulfonylactonization is depicted in Scheme 2,^{3b} which included an electrophilic addition of hypervalent iodine reagent to the double bond, and then an intramolecular nucleophilic cyclization happened, followed by another nucleophilic sulfonyloxylation. The reduced byproduct of PhI was then regenerated into hypervalent iodine reagent by the oxidation of MCPBA and used in the next reaction cycle.



Scheme 2 The possible catalytic cycle for the hypervalent iodine(III) catalyzed sulfonylactonization of alkenoic acids

In conclusion, we have successfully developed an efficient catalytic sulfonyloxylactonization of alkenoic acids using hypervalent iodine catalyst DIB and MCPBA in presence of sulfonic acids. This new protocol has some advantages such as mild reaction conditions, simple procedure, and good product yields. Furthermore, the scope of catalytic use of hypervalent iodine reagents in organic synthesis could be extended. Further investigation of the cyclizations of alkenoic acids using catalytic amounts of

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hypervalent iodine(III) reagents and MCPBA as a stoichiometric chemical oxidant will be reported in due course.

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