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Chinese Chemical Letters 20 (2009) 1427–1430
CHINESE CHEMICAL LETTERS
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A novel and facile one-pot sulfonyloxylactonization of alkenoic acids

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Received 10 April 2009

Abstract

The novel and facile one-pot method for sulfonyloxylactonization of alkenoic acids was reported: when (diacetoxyiodo)-benzene, various 4-pentenoic acids or 5-hexenoic acid and sulfonic acids were mixed in CH_2Cl_2 at room temperature, sulfonyloxylactons were obtained in good to excellent yields in short times, some had two diastereoisomers.

Keywords: Sulfonyloxylactonization; (Diacetoxyiodo)benzene; Alkenoic acid; Synthesis

Lactonizations have been studied extensively, and this type of transformation serves as an important key reaction in a variety of syntheses [1]. Among them, halolactonizations and phenylselenolactonization are general used methods [2]. Recently, organic hypervalent iodine reagents have found broad application in organic chemistry and frequently used in synthesis due to their chemical properties and reactivity are similar to those of Hg (II), Tl (III) and Pb (IV), but without the toxic and environmental problems of these heavy metal congeners [3]. Koser and co-workers first reported the tosyloxylactonization of alkenoic acids with the hypervalent iodine reagent [hydroxyl(tosyloxy)iodo]benzene (HTIB, Koser's reagent), which mechanism was different with halolactonizations and phenylselenolactonization, and received much attention [4]. The ability of HTIB to introduce the tosylate ligand into alkenoic acids prompted us to investigate the camphorsulfonyloxylactonization of alkenoic acids with the analogous reagent [hydroxyl(((+)-10-camphorsulfonyl)oxy)iodo]benzene [5], a convenient camphorsulfonyloxylactonization of alkenoic acids was found and a series of new 5-camphorsulfonyloxy-4-pentanolactones and 6-camphorsulfonyloxy-5-hexanolactone were synthesized [6]. Due to [hydroxyl(tosyloxy)iodo]benzene and [hydroxyl (((+)-10-camphorsulfonyl)oxy)iodo]benzene both were prepared from (diacetoxyiodo)benzene with respective sulfonic acid [5] and in order to extend the scope of sulfonylactonization, find simpler and more convenient sulfonylactonization, we investigated the ''one-pot'' reaction. Here we would like to report a novel and facile one-pot method for sulfonyloxylactonization of alkenoic acids

Initially, we investigated the reaction of (diacetoxyiodo)benzene (**1**) with 4-pentenoic acid (**2a**) and *p*-tosylic acid (**3a**), we found when the equal equivalent of **1**, **2a** and **3a** were mixed in CH_2Cl_2 at room temperature and stirred, the reaction was carried out fluently and finished in 1 h, the desired product 5-tosyloxy-4-pentanolactone (**4a**) was obtained in 92% yield (Scheme 1). We used (+)-10-camphorsulfonic acid (**3b**) in place of **3a**, the similar reaction also

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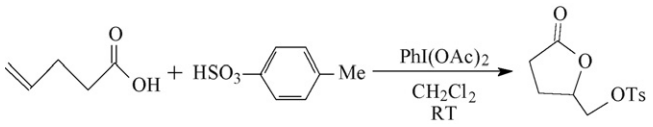
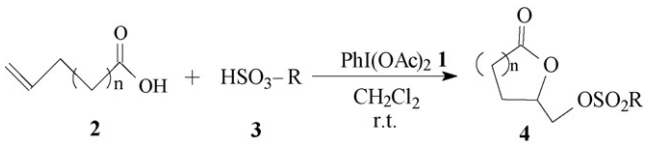
1001-8417/$ – see front matter
doi:10.1016/j.cclet.2009.06.015



Scheme 1.



Scheme 2.

gave the 5-camphorsulfonyloxy-4-pentanolactone (**7a**) in 94% yield at short time. Then various solvents were checked for the reaction, CH_2Cl_2 and CH_3CN were found to be the most preferred solvents. Under the optimum reaction conditions, the sulfonylactonization of alkenoic acids was investigated (Scheme 2), and the good results are summarized in Table 1.

From Table 1, it is notable that various 4-pentenoic acids can react with (diacetoxyiodo)benzene and *p*-tosylic acid or (+)-10-camphorsulfonic acid fast and convenient, gave the corresponding sulfonyloxylactons in excellent yields

Table 1
The result of the sulfonylactonization of alkenoic acids.

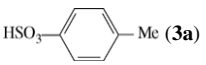
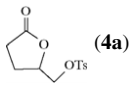
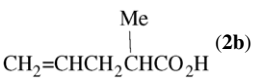
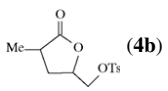
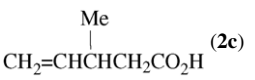
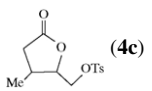
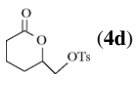
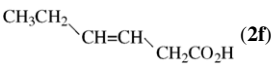
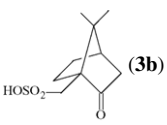
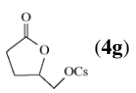
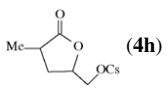
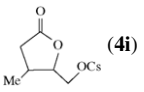
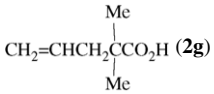
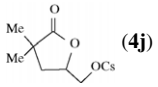
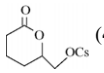
Entry	Alkenoic acids (2)	Sulfonic acid (3)	Sulfonyloxylactones (4)[a]	Time (h)	Yield (%)[b]
1	$CH_2{=}CH(CH_2)_2CO_2H$ (**2a**)	 (**3a**)	 (**4a**)	1	92
2	 (**2b**)	**3a**	 (**4b**)	1.5	97 (2.7:1)
3	 (**2c**)	**3a**	 (**4c**)	2	93 (1.7:1)
4	$CH_2{=}CH(CH_2)_3CO_2H$ (**2d**)	**3a**	 (**4d**)	3	76
5	$CH_2{=}CHCH_2CO_2H$ (**2e**)	**3a**	 (**4e**)	100	70
6	 (**2f**)	**3a**	 (**4f**)	100	38
7	**2a**	 (**3b**)	 (**4g**)	2	94
8	**2b**	**3b**	 (**4h**)	2	98 (2.8:1)

Table 1 (*Continued*)

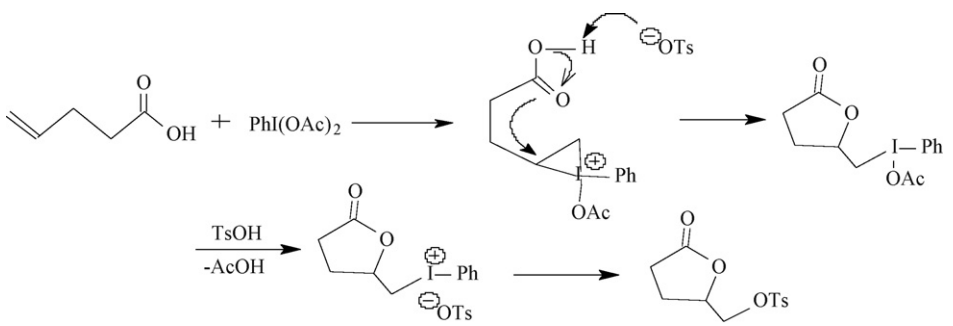
Entry	Alkenoic acids (2)	Sulfonic acid (3)	Sulfonyloxylactones (4)[a]	Time (h)	Yield (%)[b]
9	**2c**	**3b**	 **(4i)**	2.5	90 (1.9:1)
10	 **(2g)**	**3b**	 **(4j)**	2	91
11	**2d**	**3b**	 **(4k)**	3.5	85
12	**2e**	**3b**	**4e**	90	65
13	**2f**	**3b**	**4f**	45	40

[a] Ts, *p*-Me-$C_6H_4SO_2$; Cs, (+)-10-camphorylsulfonyl.
[b] Isolated yield.

(entries 1–3, 7–10). Similar treatment of 5-hexenoic acid, it needed somewhat longer time compared with **2a**, providing 6-tosyloxy-5-hexanolactone in middle yield (entry 4) and 6-camphorsulfonyloxy-5-hexanolactone in good yield (entry 11), which meant that five member ring lactones were formed easier than six member ring lactones in the sulfonyloxylactonization. When 3-butenoic acid and trans-3-hexenoic acid were treated in same reaction conditions, the reaction was difficult to carry out and after long time it gave unsaturated lactones (entries 5, 6, 12, 13), not the desired sulfonylactons. It was found by ^{1}H NMR technique that the desired 3-sulfonyloxy-4-butanolactones were first formed, which then transformed into the unsaturated lactones during workup procedure by elimination. Compared with 3-butenoic acid, trans-3-hexenoic acid gave lower yields is due to the resistance effect of ethyl group (entries 6, 13).

Koser and co-workers in 1988 reported another lactonizaton using the hypervalent iodine reagent [hydroxyl((bis(phenyloxy)phosphoryl)oxy)iodo]benzene, and they found when 2-methyl-4-pentenoic acid (**2b**) was treated with the hypervalent iodine reagent, the products were a mixture of diastereomers, the ratios were varied form 1.2 to 1.4:1 [7]. In our reaction protocol, we also found when **2b** was used, the corresponding 5-sulfonyloxy-4-pentanolactones were mixtures of diastereomers, the ratios varied from 2.7:1 for *p*-tosylic acid to 2.8:1 for camphorsulfonylic acid respectively, which were determined by examination of the ^{1}H NMR spectrum of sulfonylactons; while 3-methyl-4-pentenoic acid (**2c**) was treated in the reaction, the ratios for the obtained mixtures of diastereomers were 1.7:1 and 1.9:1 for *p*-tosylic acid and camphorsulfonylic acid respectively, which were somewhat lower compared with **2b**. Besides **2b** and **2c**, we also checked other alkenoic acids, not observed them having the stereoselectivity in the sulfonylactonization at room temperature.

The proposed mechanism for the one-pot sulfonylactonization of alkenoic acids is similar to the literature procedure (Scheme 3) [4], which included the electrophilic addition of hypervalent iodine reagent on the alkene, then



Scheme 3.

an intramolecular nucleophilic displacement was happened, followed by another nucleophilic displacement to give the sulfonylactone.

A typical procedure for the sulfonyloxylactonization of alkenoic acids. To CH_2Cl_2 (2 mL), alkenoic acid **2** (0.3 mmol), (diacetoxyiodo)benzene **1** (0.3 mmol) and sulfolic acid **3** (0.3 mmol) were added. The mixture was stirred at room temperature for several hours (shown in Table 1) and then separated on a silica gel plate using (hexane–ethyl acetate 2:1) as eluant to give sulfonyloxylacton **4** in good to excellent yields.

In conclusion, we have successfully developed a novel and convenient reaction of (diacetoxyiodo)benzene with alkenoic acids and sulfonic acids, several 5-sulfonyloxy-4-pentanolactones in excellent yields and 6-sulfonyloxy-5-hexanolactones in middle to good yields were prepared. The one-pot sulfonylactonization has some advantages such as mild reaction conditions, simple procedure and good yields. Furthermore, the scope of hypervalent iodine reagents in organic synthesis could be extended.

Acknowledgments

Financial support from the National Science Foundation of China (No. 20672100) and Zhejiang Province Natural Science Foundation of China (No. Y4080068) are greatly appreciated.

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