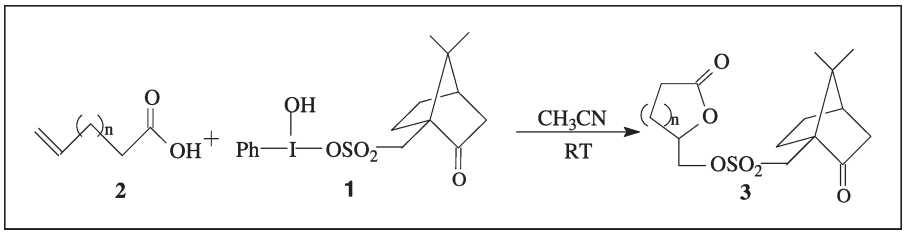
Min Zhu,[a]* Na-Bo Sun,[a] He Li,[a] and Jie Yan[b]

[a]College of Biological and Environmental Sciences, Zhejiang Shuren University, Hangzhou, Zhejiang 310015, People's Republic of China
[b]College of Chemical Engineering and Materials Sciences, Zhejiang University of Technology, Hangzhou, Zhejiang 310032, People's Republic of China
*E-mail: hzzm60@163.com
Received September 3, 2009
DOI 10.1002/jhet.337
Published online 4 March 2010 in Wiley InterScience (www.interscience.wiley.com).



The novel reaction of [hydroxyl (((+)-10-camphorsulfonyl)oxy)iodo]benzene (1) with alkenoic acids was reported. When **1** reacted with various 4-pentenoic acids in CH_3CN, camphorsulfonylactons were obtained in excellent yields in short times, some had two diastereoisomers, whereas **1** reacted with 5-hexenoic acid, giving middle yield of camphorsulfonylacton; however, 3-butenoic and *trans*-3-hexenoic acids reacted with **1** slowly in CH_2Cl_2, only unsaturated lactones were provided.

J. Heterocyclic Chem., **47**, 436 (2010).

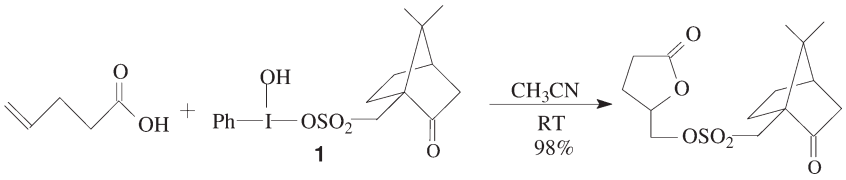
INTRODUCTION

Lactonizations have been studied extensively, and this type of transformation serves as an important key reaction in a variety of syntheses [1]. Among them, halolactonization 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 coworkers 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 halolactonization 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 (1) [5], a stable and incorporating a chiral ligand hypervalent iodine reagent. Here, we would like to report a novel and convenient camphorsulfonyloxylactonization of alkenoic acids, a series of new 5-camphorsulfonyloxy-4-pentanolactones and 6-camphorsulfonyloxy-5-hexanolactone were synthesized.

Initially, we prepared [hydroxyl (((+)-10-camphorsulfonyl)oxy)iodo]benzene (1) according to the literature procedure [5]. Then, we investigated the reaction of 4-pentenoic acid with **1**, we found that when the equal equivalent of both them were mixed and stirred in CH_3CN at room temperature, the reaction was carried out fluently and finished in 0.5 h, the novel compound of 5-camphorsulfonyloxy-4-pentanolactone was obtained in nearly quantitative (Scheme 1). Prompted by the good result, a series of experiments were performed on the reaction of 4-pentenoic acid with **1** in order to determine the suitable reaction conditions, and CH_3CN and CH_2Cl_2 were found to be the most preferred solvents. Finally, the reaction of a series of alkenoic acids (2) with **1** in CH_3CN or CH_2Cl_2 at room temperature were investigated, several new camphorsulfonylactons (3) were provided (Scheme 2), the good results are summarized in Table 1.

It is shown from Table 1 that 4-pentenoic acid (2a), 2-methyl-4-pentenoic acid (2b), 3-methyl-4-pentenoic acid (2c) and 2, 2-dimethyl-4-pentenoic acid (2d) all reacted with **1** fast, and gave the corresponding 5-camphorsulfonyloxy-4-pentanolactones, respectively, in excellent yields (entries **1–4**); Similar treatment of 5-hexenoic acid needed longer time compared with 4-pentenoic acid and provided 6-camphorsulfonyloxy-5-hexanolactone (3e) in middle yield (entry **5**), which meant that five-membered lactone ring was formed easier than six-membered lactone ring in the camphorsulfonyloxylactonization of alkenoic acids. We also checked the reaction of 6-heptenoic acid with **1**, found that after 48 h it had not been completed and the desired seven-membered lactone ring was obtained in poor yield. When 3-butenoic and *trans*-3-hexenoic acids were treated with **1**

Scheme 1



in same reaction conditions, the reaction was somewhat difficult to carry out in CH_3CN and slowly; then using CH_2Cl_2 in place of CH_3CN, we found that after 24 h the reaction was finished. However, the products were not the desired camphorsulfonylactons, two unsaturated lactones were found (entries **6** and **7**). It was revealed by ^{1}H-NMR technique that the desired 3-sulfonyloxy-4-butanolactones were first formed, but then transformed into the unsaturated lactones during workup procedure by elimination. 2-Cyclopenteneacetic acid reacted with **1** also fluently, but gave another unsaturated lactone (entry **8**), which agreed with Koser and coworkers report [4].

Koser et al. in 1988 reported another lactonizaton using the similar hypervalent iodine reagent, [hydroxyl ((bis(phenyloxy)phosphoryl)oxy)iodo]benzene, and they found that when 2-methyl-4-pentenoic acid 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 [6]. Because of [hydroxyl (((+)-10-camphorsulfonyl)oxy)-iodo]benzene is a chiral hypervalent iodine reagent, the lactonizaton of it may be stereoselectivity, and some evidence was obtained by examination of the ^{1}H-NMR spectrum of camphorsulfonylactons: when 2-methyl-4-pentenoic acid (2b) and 3-methyl-4-pentenoic acid (2c) were treated with **1** at room temperature, the provided products were mixtures of diastereomers, the ratios of them were 3.1:1 and 2.3:1, respectively. Then, we checked the effect of temperature on the stereoselectivity of **2b** and found that the camphorsulfonylactonization got diastereomers with higher ratio at lower of temperature; The reaction was investigated at room temperature, -20°C and -50°C, respectively, the ratios of diastereomers varied from 3.1, 4.0 to 4.8:1. However, except **2b** and **2c**, other alkenoic acids were not observed having the stereoselectivity in the camphorsulfonylactonization at room temperature. Solvents also had small effect on the stereoselectivity, we found that CH_3CN was better than CH_2Cl_2 to get high diastereomers ratio for **2b** in the reaction.

[Hydroxyl (((+)-10-camphorsulfonyl)oxy)iodo]benzene was made from (diacetoxyiodo)benzene and (+)-10-camphorsulfonic acid in CH_3CN. To extend the scope of camphorsulfonylactonization, find simpler and more convenient camphorsulfonylactonization, the ''one-pot'' reaction was investigated; when equal equivalent of (diacetoxyiodo)benzene, (+)-10-camphorsulfonic acid and 4-pentenoic acid were mixed in CH_3CN at room temperature and stirred the mixture, we found that the reaction was completed in 0.5 h, giving the desired **3a** in 95% of yield. When [bis(trifluoroacetoxy)iodo]benzene was used in place of (diacetoxyiodo)benzene, the same result was obtained in 94% of yield. Therefore, the simpler and more convenient ''one-pot'' camphorsulfonylactonization was found (Scheme 3). Further investigation of the reaction will be reported later.

The plausible mechanism is similar to the literature procedure [4], which included the electrophilic addition of hypervalent iodine reagent **1** on the alkene, then an intramolecular nucleophilic displacement was happened, followed by another nucleophilic displacement to give the camphorsulfonylactone (Scheme 4).

In conclusion, we have successfully developed a novel and convenient reaction of [hydroxyl-(((+)-10-camphorsulfonyl)oxy)iodo]benzene with alkenoic acids, several new 5-camphorsulfonyloxy-4-pentanolactones in excellent yields and 6-camphorsulfonyloxy-5-hexanolactone in middle yield were prepared. The camphorsulfonylactonization 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.

Scheme 2

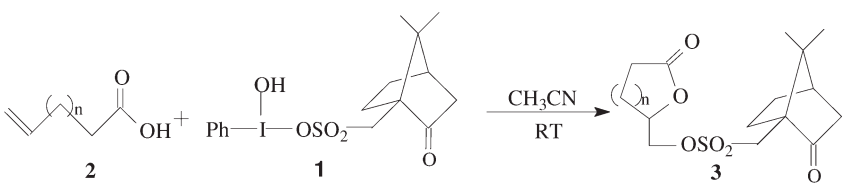
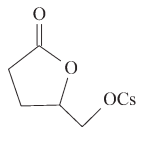
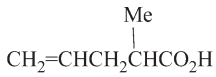
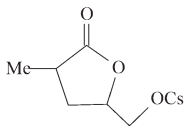
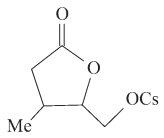
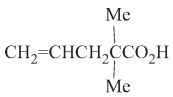
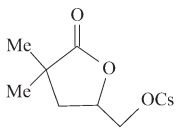
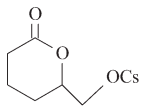
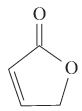
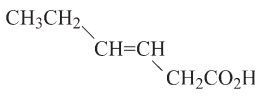
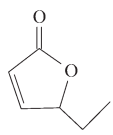
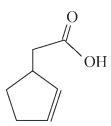
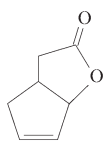


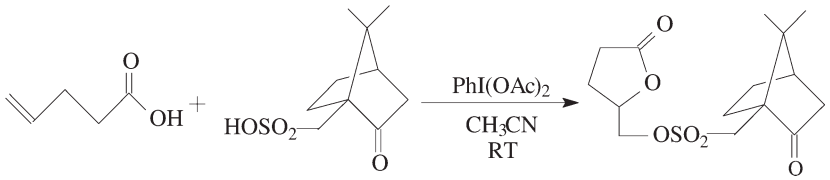
Table 1

The result of the camphorsulfonylactonization of alkenoic acids.

Entry	Alkenoic acids (2)	Camphorsulfonyloxylactones (3)[a]	Time (h)	Yield (%)[b]
1	$CH_2=CH(CH_2)_2CO_2H$ **2a**	 **3a**	0.5	98
2	 **2b**	 **3b**	0.5	95
3	 **2c**	 **3c**	0.5	93
4	 **2d**	 **3d**	1.0	95
5	$CH_2=CH(CH_2)_3CO_2H$ **2e**	 **3e**	2.5	63
6	$CH_2=CHCH_2CO_2H$ **2f**	 **3f**	24	52[c]
7	 **2g**	 **3g**	24	41[c]
8	 **2h**	 **3h**	1.0	81

[a] Cs, (+)-10-camphorylsulfonyl.
[b] Isolated yield.
[c] CH_2Cl_2 was used as solvent.

Scheme 3



EXPERIMENTAL

General procedure for the iodination of terminal alkynes. To CH_3CN or CH_2Cl_2 (2 mL), alkenoic acid **2** (0.3 mmol), [hydroxyl (((+)-10-camphorsulfonyl)oxy)iodo]benzene **1** (0.3 mmol) were added. The mixture was stirred at room temperature for 0.5–24 h (shown in Table 1) and then separated on a silica gel plate using (3:1, hexane–ethyl acetate) as eluant to give camphorsulfonyloxylacton **3** in good to excellent yields.

3a: Oil. ^{1}H-NMR (500 MHz, $CDCl_3$): 4.82–4.79 (m, 1H), 4.51 (ddd, J = 22.0, 11.5, 3.0 Hz, 1H), 4.37 (ddd, J = 21.5, 11.0, 4.5 Hz, 1H), 3.62 (dd, J = 15.5, 6.0 Hz, 1H), 3.08 (dd, J = 15.0, 4.0 Hz, 1H), 2.69–2.52 (m, 2H), 2.43–2.37 (m, 3H), 2.20–2.02 (m, 3H), 1.97 (d, J = 17.5 Hz, 1H), 1.75–1.65 (m, 1H), 1.51–1.45 (m, 1H), 1.10 (s, 3H), 0.88 (s, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$): 214.2, 176.1, 76.7 (d, J = 7.5 Hz), 70.1, 69.9, 57.8 (d, J = 2.5 Hz), 48.1, 47.2, 42.6 (d, J = 2.5 Hz), 42.4 (d, J = 1.3 Hz), 27.9, 26.8, 24.8 (d, J = 7.5 Hz), 23.3 (d, J = 8.8 Hz), 19.5 (t, J = 2.5 Hz). IR (film): ν = 2963, 1781, 1746, 1456, 1418, 1360, 1282, 1167, 1070, 962 cm^{-1}. MS (EI, *m*/*z*, %): 330 (M^+, 100). HRMS: $C_{15}H_{22}O_6S$ calcd.: 330.1137, found: 330.1125.

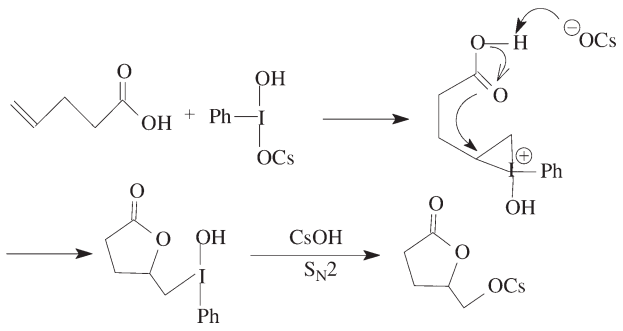
3b: Oil. ^{1}H-NMR (500 MHz, $CDCl_3$): 4.79–4.72 (**3b$_1$**) and 4.68–4.62 (**3b$_2$**) (m, 1H), 4.51 (ddd, J = 19.0, 11.5, 3.0 Hz, 1H), 4.37–4.31 (m, 1H), 3.66–3.59 (m, 1H), 3.09–3.03 (m, 1H), 2.83–2.78 (**3b$_1$**) and 2.77–2.70 (**3b$_2$**) (m, 1H), 2.56–2.49 (m, 1H), 2.46–2.37 (m, 2H), 2.16–2.13 (m, 1H), 2.10–2.03 (m, 1H), 1.97 (d, J = 18.0 Hz, 1H), 1.79–1.68 (m, 2H), 1.50–1.44 (m, 1H), 1.31 (d, J = 5.5 Hz, **3b$_1$**) and 1.30 (d, J = 6.0 Hz, **3b$_2$**) (d, 3H), 1.10 (**3b$_1$**) and 1.09 (**3b$_2$**) (s, 3H), 0.89 (**3b$_1$**) and 0.88 (**3b$_2$**) (s, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$): 214.4, 214.3, 179.2, 178.3, 74.9, 74.5 (d, J = 7.5 Hz), 70.5, 70.4, 69.7, 69.4, 57.9 (d, J = 3.8 Hz), 48.2 (d, J = 3.8 Hz), 47.4, 47.3 (d, J = 6.3 Hz), 42.7, 42.5 (d, J = 2.5 Hz), 35.2, 33.7, 32.2 (d, J = 8.8 Hz), 31.6 (d, J = 6.3 Hz), 26.9, 24.9 (t, J = 3.8 Hz), 19.6 (d, J = 5.0 Hz), 16.1, 15.1 (d, J = 3.8 Hz). IR (film): ν = 2966, 1775, 1747, 1456, 1360, 1286, 1168, 1069, 972, 931 cm^{-1}. MS (EI, *m*/*z*, %): 344 (M^+, 100). HRMS: $C_{16}H_{24}O_6S$ calcd.: 344.1294, found: 344.1289.

3c: Oil. ^{1}H-NMR (500 MHz, $CDCl_3$): 4.75–4.30 (m, 3H), 3.63 (dd, J = 15.0, 4.5 Hz, 1H), 3.07 (dd, J = 15.5, 4.0 Hz, 1H), 2.85–2.78 (m, 1H), 2.72–2.66 (**3c$_1$**) and 2.56–2.49 (**3c$_2$**) (m, 1H), 2.45–2.22 (m, 3H), 2.15–2.13 (m, 1H), 2.11–2.02 (m, 1H), 1.97 (d, J = 18.5 Hz, 1H), 1.75–1.65 (m, 1H), 1.51–1.44 (m, 1H), 1.23 (dd, J = 6.5, 3.0 Hz, **3c$_1$**) and 1.17 (d, J = 7.5 Hz, **3c$_2$**) (3H), 1.10 (s, 3H), 0.88 (s, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$): 214.3, 175.7(d, J = 2.5 Hz), 175.4, 83.3 (d, J = 2.5 Hz), 79.2 (d, J = 5.0 Hz), 68.8, 68.6, 68.2, 68.0, 57.9 (d, J = 3.8 Hz), 48.2, 47.4 (d, J = 3.8 Hz), 47.2 (d, J = 2.5 Hz), 42.7 (d, J = 3.8 Hz), 42.5 (d, J = 2.5 Hz), 36.4 (d, J = 3.8 Hz), 36.2, 31.9, 31.8, 31.7, 26.9, 24.9 (d, J = 2.5 Hz), 24.8, 19.6 (d, J = 3.8 Hz), 18.0, 13.5. IR (film): ν = 2965, 1785, 1747, 1456, 1418, 1361, 1283, 1214, 1166, 1054, 975, 933 cm^{-1}. MS (EI, *m*/*z*, %): 344 (M^+, 100). HRMS: $C_{16}H_{24}O_6S$ calcd.: 344.1294, found: 344.1277.

3d: Oil. ^{1}H-NMR (500 MHz, $CDCl_3$): 4.73–4.69 (m, 1H), 4.51 (ddd, J = 20.0, 11.5, 3.5 Hz, 1H), 4.33 (ddd, J = 19.5, 11.5, 5.5 Hz, 1H), 3.63 (dd, J = 15.5, 8.0 Hz, 1H), 3.08 (d, J = 15.0 Hz, 1H), 2.45–2.37 (m, 2H), 2.20–2.13 (m, 2H), 2.10–2.01 (m, 1H), 1.99–1.95 (m, 2H), 1.75–1.67 (m, 1H), 1.51–1.45 (m, 1H), 1.32 (s, 3H), 1.30 (s, 3H), 1.10 (s, 3H), 0.89 (s, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$): 214.3 (d, J = 8.8 Hz), 180.8, 73.6 (d, J = 3.8 Hz), 69.9, 69.6, 57.9, 48.2, 47.4 (d, J = 10.0 Hz), 42.7, 42.5 (d, J = 2.5 Hz), 40.0 (d, J = 2.5 Hz), 38.4 (d, J = 7.5 Hz), 26.9, 24.9 (d, J = 3.8 Hz), 24.8 (d, J = 3.8 Hz), 24.7 (d, J = 2.5 Hz), 19.6. IR (film): ν = 2967, 1775, 1747, 1457, 1361, 1280, 1207, 1169, 1130, 1067, 983, 926 cm^{-1}. MS (EI, *m*/*z*, %): 358 (M^+, 100). HRMS: $C_{17}H_{26}O_6S$ calcd.: 358.1451, found: 358.1441.

3e: Oil. ^{1}H-NMR (500 MHz, $CDCl_3$): 4.65–4.55 (m, 1H), 4.45–4.34 (m, 2H), 3.64 (dd, J = 15.0, 8.5 Hz, 1H), 3.09 (d, J = 15.0 Hz, 1H), 2.65–2.60 (m, 1H), 2.52–2.35 (m, 3H), 2.15–1.85 (m, 6H), 1.80–1.70 (m, 2H), 1.51–1.42 (m, 1H), 1.10 (s, 3H), 0.89 (s, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$): 214.4, 170.1, 70.4, 70.2, 57.9, 48.2 (d, J = 2.5 Hz), 47.4 (d, J = 2.5 Hz), 42.7 (d, J = 3.8 Hz), 42.5, 29.5, 26.9, 24.9 (d, J = 11.3 Hz), 23.9 (d, J = 6.3 Hz), 19.6, 18.2. IR (KBr): ν = 2961, 1744, 1456, 1360, 1240, 1169, 1081, 1054, 963 cm^{-1}. MS (EI, *m*/*z*, %): 344 (M^+, 100). HRMS: $C_{16}H_{24}O_6S$ calcd: 344.1294, found: 344.1288.

Scheme 4



Acknowledgments. Financial support from the Natural Science Foundation of China (Project 20672100) is greatly appreciated.

REFERENCES AND NOTES

[1] (a) Dowle, M. D.; Davies, D. I. Chem Soc Rev 1979, 8, 171; (b) Harding, K. E.; Tiner, T. H. In Comprehensive Organic Synthesis; Trost, B. M., Fleming, I., Eds.; Pergamon Press: Oxford, 1991; Vol. 4, p 363; (c) Rousseau, G.; Robin, S. Tetrahedron 1998, 54, 13681.

[2] (a) Bartlett, P. A.; Meyerson, J. J Am Chem Soc 1978, 100, 3950; (b) Haas, J.; Piguel, S.; Wirth, T. Org Lett 2002, 4, 297; (c) Nicolaou, K. C.; Seitz, S. P.; Sipio, W. J.; Blount, J. F. J Am Chem Soc 1979, 101, 3884.

[3] (a) Varvoglis, A. Tetrahedron 1997, 53, 1179; (b) Stang, P. J.; Zhdankin, V. V. Chem Rev 1996, 96, 1123; (c) Zhdankin, V. V.; Stang, P. J. Chem Rev 2002, 102, 2523; (d) Wirth, T.; Hirt, U. H. Synthesis 1999, 1271; (e) Kirschning, A. Eur J Org Chem 1998, 11, 2267; (f) Ochiai, M. J Organomet Chem 2000, 611, 494; (g) Okuyama, T. Acc Chem Res 2002, 35, 12; (h) Zhdankin, V. V.; Stang, P. J. Tetrahedron 1998, 54, 10927; (i) Grushin, V. V. Chem Soc Rev 2000, 29, 315.

[4] Shah, M.; Taschner, M. J.; Koser, G. F.; Rach, N. L. Tetrahedron Lett 1986, 27, 4557.

[5] Hatzigrigoriou, E.; Varvoglis, A.; Bakola-Christianopoulou, M. J Org Chem 1990, 55, 315.

[6] Koser, G. F.; Lodaya, J. S.; Ray, D. G., III; Kokil, P. B. J Am Chem Soc 1988, 110, 2987.