Tetrahedron Letters 51 (2010) 2480–2482

Contents lists available at ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

# A convenient phosphoryloxylactonization of pentenoic acids with catalytic hypervalent iodine(III) reagent

Zhong-Shi Zhou [a,*], Xue-Han He [b]

[a] College of Biological and Environmental Sciences, Zhejiang Shuren University, Hangzhou 310015, PR China
[b] Zhejiang Institute of Geology and Mineral Resource Laboratory, Hangzhou 310007, PR China

ARTICLE INFO

*Article history:*
Received 19 January 2010
Revised 21 February 2010
Accepted 26 February 2010
Available online 3 March 2010

ABSTRACT

A novel and convenient catalytic method for phosphoryloxylactonization of pentenoic acids is available: the cyclization of 4-pentenoic acids with phosphates using iodobenzene as a recyclable catalyst in combination with *m*-chloroperbenzoic acid as the terminal oxidant was easily carried out in $CF_3CH_2OH$ at room temperature, giving phosphoryloxylactons in good yields, some of them had two diastereoisomers.

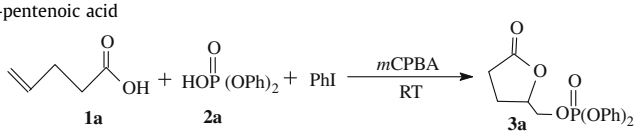


Organic hypervalent iodine reagents have been receiving much attention due to their low toxicity, mild reactivity, ready availability, high stability, easy handing, etc. and have found broad application in organic chemistry as alternatives replacing the highly toxic Hg(II), Tl(III), and Pb(IV) heavy-metal oxidants.[1] They are usually used as stoichiometric oxidants in synthesis and after the reactions, the at least equimolar amounts of iodoarenes are produced as by-products, most of them are disposed of and are not well utilized, which restricts their more applications. In 2005, Ochiai's group and Kita's group independently reported the improvement of using catalytic hypervalent iodine reagents in synthesis,[2] which was economical, environmentally friendly, and has led to recent new applications of catalytic hypervalent iodine reagents in organic chemistry.[3] In these catalytic reactions, a catalytic amount of iodoarene together with a stoichiometric oxidant is used. The oxidant generates the hypervalent iodine reagent in situ, and after the oxidative transformation, the reduced iodoarene is re-oxidized. Iodobenzene (PhI) is the most utilized iodoarene, *m*-chloroperbenzoic acid (*m*CPBA) and Oxone® are usually used as the terminal oxidants.

Koser and co-workers first reported the phosphoryloxylactonization of alkenoic acids with the hypervalent iodine reagent, [hydroxyl((bis(phenyloxy)phosphoryl)oxy)iodo]benzene, and some phosphoryloxylactones were obtained in the preparation.[4] However, after the report there is no other Letter about the phosphoryloxylactonization been published and the numbers of phosphoryloxylactones are only a few. In order to extend the scope of catalytic use of hypervalent iodine reagents in organic synthesis, and to find a convenient method to prepare more and important phosphoryloxylactones, we have investigated the phosphoryloxylactonization of pentenoic acids with catalytic hypervalent iodine(III) reagent. Here we would like to report the convenient and catalytic phosphoryloxylactonization of alkenoic acids, a series of new 5-phosphoryloxy-4-pentanolactones were synthesized.

We first examined the reaction of equal equivalent of 4-pentenoic acid, diphenyl phosphate, and *m*CPBA with 0.1 equiv of iodobenzene in $CF_3CH_2OH$ at room temperature, and found that the

**Table 1**
Optimization of the hypervalent iodine(III)-catalyzed phosphoryloxylactonization of 4-pentenoic acid



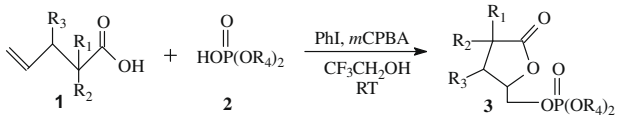

1a 2a 3a

| Entry | PhI (equiv) | *m*CPBA (equiv) | Diphenyl phosphate (equiv) | Solvent | Time (h) | Yield[a] (%) |
|---|---|---|---|---|---|---|
| 1 | 0.1 | 1 | 1 | $CF_3CH_2OH$ | 24 | 65 |
| 2 | 0.1 | 1 | 1 | $CH_2Cl_2$ | 24 | 40 |
| 3 | 0.1 | 1 | 1 | $CH_3CN$ | 24 | 31 |
| 4 | 0.1 | 1 | 1 | THF | 24 | 10 |
| 5 | 0.1 | 1 | 1 | $CH_3OH$ | 24 | 18 |
| 6 | 0.1 | 1 | 1 | DMF | 24 | 6 |
| 7 | 0.1 | 1 | 1 | $CF_3CH_2OH$ | 2 | 32 |
| 8 | 0.1 | 1 | 1 | $CF_3CH_2OH$ | 4 | 48 |
| 9 | 0.1 | 1 | 1 | $CF_3CH_2OH$ | 8 | 65 |
| 10 | 0.1 | 1 | 1 | $CF_3CH_2OH$ | 16 | 64 |
| 11 | 0.1 | 1 | 1 | $CF_3CH_2OH$ | 48 | 64 |
| 12 | 0.1 | 2 | 2 | $CF_3CH_2OH$ | 24 | 63 |
| 13 | 0.05 | 1 | 1 | $CF_3CH_2OH$ | 8 | 54 |
| 14 | 0 | 1 | 1 | $CF_3CH_2OH$ | 24 | 0 |
| 15 | 0.1 | Oxone® (1) | 1 | $CF_3CH_2OH$ | 24 | 5 |
| 16 | 0.1 | $NaBO_3$ (1) | 1 | $CF_3CH_2OH$ | 24 | 3 |
| 17 | 0.1 | $Na_2S_2O_8$ (1) | 1 | $CF_3CH_2OH$ | 24 | 6 |

[a] Isolated yields.

* Corresponding author. Tel.: +86 571 88297172; fax: +86 571 88297099.
*E-mail address:* zhoushan@hz.zj.cn (Z.-S. Zhou).

0040-4039/$ - see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetlet.2010.02.153




**Scheme 1.**

reaction was carried out easily and the desired product of 5-(bis(phenyloxy)phosphory)oxy-4-pentanolactone was obtained (**3a**) in 65% yield in 24 h. Then, the reaction conditions were optimized, and the results are summarized in Table 1. As a suitable solvent, $CF_3CH_2OH$ was the most preferred (entries 1–6). The reaction time was influential, the yield of **3a** was increased from 2 to 8 h and 8 h was the best suitable reaction time (entries 1, 7–11). When 2 equiv of diphenyl phosphate and *m*CPBA was used, the yield of **3a** was not changed (entries 1 and 12). The amount of catalyst of PhI was influential (entries 9, 13 and 14), and 0.1 equiv was the best choice. Other oxidants such as Oxone®, $NaBO_3$, and $Na_2S_2O_8$ were also not successful (entries 15–17).

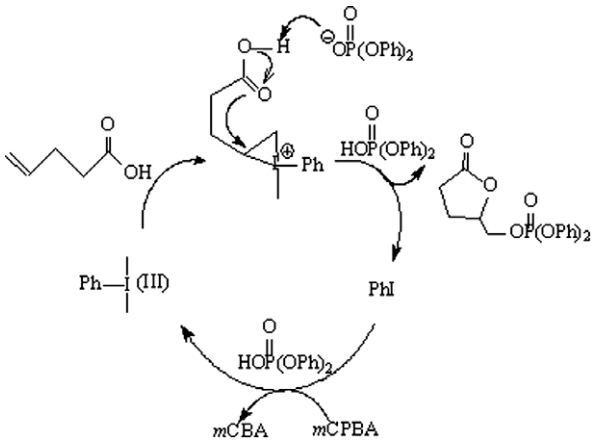
Under the optimum reaction conditions, we investigated the catalytic phosphoryloxylactonization of equal equivalent of alkenoic acids (**1**), phosphate (**2**), and *m*CPBA with 0.1 equiv of PhI in $CF_3CH_2OH$ at room temperature in 8 h (Scheme 1), the results are summarized in Table 2.

It is notable that the good yields of 5-phosphoryloxy-4-pentanolactones (**3**) were obtained for a series of 4-pentenoic acids (**1**) (entries 1–7). When dibenzyl phosphate (**2b**) was used, the yields of the corresponding 5-phosphoryloxy-4-pentanolactones were higher than that of diphenyl phosphate (**2a**). It was found that bis(4-nitrophenyl)phosphate (**2c**) also reacted with 4-pentenoic acid, but the product (3h) was unstable and decomposed during purification (entry 8). Similar treatment of 3-butenoic acid and 2-cyclopentene-1-acetic acid with **2a** did not provide the desired phosphoryloxylactones, only the unsaturated lactone 2(5*H*)-furanone from 3-butenoic acid and tetrahydro-cyclopenta[*b*]furan-2-one from 2-cyclopentene-1-acetic acid was obtained in moderate yields. In order to prepare six-membered phosphoryloxylactone, we also checked the reaction of 5-hexenoic acid with **2a** and found that the desired product was first formed, but decomposed during

**Table 2**
The result of the phosphoryloxylactonization of alkenoic acids

| Entry | Alkenoic acids (**1**) | Phosphates (**2**) | Phosphoryloxylactones (**3**) | Yield[a] (%) |
|---|---|---|---|---|
| 1 | $CH_2{=}CH(CH_2)_2CO_2H$ **1a** | $HOP(OPh)_2$ **2a** | **3a** | 65 |
| 2 | $CH_2{=}CHCH_2CH(Me)CO_2H$ **1b** | **2a** | **3b** | 63 |
| 3 | $CH_2{=}CHCH(Me)CH_2CO_2H$ **1c** | **2a** | **3c** | 64 |
| 4 | $CH_2{=}CHCH_2C(Me)_2CO_2H$ **1d** | **2a** | **3d** | 66 |
| 5 | **1a** | $HOP(OBn)_2$ **2b** | **3e** | 70 |
| 6 | **1b** | **2b** | **3f** | 71 |
| 7 | **1d** | **2b** | **3g** | 73 |
| 8 | **1a** | $HOP(OC_6H_4NO_2\text{-}p)_2$ **2c** | **3h** | 58[b] |

[a] Isolated yields.
[b] $^1H$ NMR analysis.




**Scheme 2.**

workup procedure by $^1$H NMR technique, which agreed with Koser' report that the six-membered phosphoryloxylacton was unstable.[4] Phosphoryloxylactones **3b**, **3c,** and **3f** were mixtures of diastereomers; the ratios were 3.0:1 for **3b**, 1.1:1 for **3c**, and 2.7:1 for **3f**, respectively, which were determined by examination of the $^1$H NMR spectra of phosphoryloxylactons.

The proposed mechanism for the catalytic cycle of phosphoryloxylactonization is shown in Scheme 2,[5] which included the electrophilic addition of hypervalent iodine reagent on the double bond, and then an intramolecular nucleophilic cyclization happened, followed by another nucleophilic substitution. PhI was generated into hypervalent iodine reagent by the oxidation of *m*CPBA and was used in the cycle.

A typical procedure for the catalytic phosphoryloxylactonization of alkenoic acids: alkenoic acid **1a** (0.3 mmol), diphenyl phosphate **2a** (0.3 mmol), *m*CPBA (75%, 0.3 mmol), and iodobenzene (0.03 mmol) were added in $CF_3CH_2OH$ (2 mL). The mixture was stirred at room temperature for 8 h and then water (5 mL), satd aq $Na_2S_2O_3$ (2 mL), and satd aq $Na_2CO_3$ (2 mL) were added. The mixture was extracted with $CH_2Cl_2$ ($2 \times 5$ mL), the combined organic layer was washed with brine, dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified on a silica gel plate using (3:2 hexane–ethyl acetate) as an eluant to give 5-(bis(phenyloxy)phosphory)oxy-4-pentanolactone (**3a**) in 65% of yield.

In summary, we have successfully developed a convenient catalytic phosphoryloxylactonization of pentenoic acids, several 5-phosphoryloxy-4-pentanolactones in good yields were prepared. This method 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.

## Acknowledgment

Financial support from the Zhejiang Province Natural Science Foundation of China (Project Y4080068) is greatly appreciated.

## References and notes

1. (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) Kirschning, A. *Eur. J. Org. Chem.* **1998**, *11*, 2267; (e) Ochiai, M. *J. Organomet. Chem.* **2000**, *611*, 494; (f) Okuyama, T. *Acc. Chem. Res.* **2002**, *35*, 12; (g) Zhdankin, V. V.; Stang, P. J. *Tetrahedron* **1998**, *54*, 10927; (h) Grushin, V. V. *Chem. Soc. Rev.* **2000**, *29*, 315.
2. (a) Ochiai, M.; Takeuchi, Y.; Katayama, T.; Sueda, T.; Miyamoto, K. *J. Am. Chem. Soc.* **2005**, *127*, 12244; (b) Dohi, T.; Maruyama, A.; Yoshimura, M.; Morimoto, K.; Tohma, H.; Kita, Y. *Angew. Chem., Int. Ed.* **2005**, *44*, 6193.
3. (a) Dohi, T.; Kita, Y. *Kagaku* **2006**, *61*, 68; (b) Richardson, R. D.; Wirth, T. *Angew. Chem., Int. Ed.* **2006**, *45*, 4402; (c) Dohi, T.; Minamitsuji, Y.; Maruyama, A.; Hirose, S.; Kita, Y. *Org. Lett.* **2008**, *10*, 3559; (d) Ochiai, M. *Chem. Rec.* **2007**, *7*, 13; (e) Uyanik, M.; Ishihara, K. *Chem. Commun.* **2009**, 2086; (f) Dohi, T.; Kita, Y. *Chem. Commun.* **2009**, 2073; (g) Liu, H.-G.; Tan, C.-H. *Tetrahedron Lett.* **2007**, *48*, 8220; (h) Yan, J.; Wang, H.; Yang, Z. P.; He, Y. *Synlett* **2009**, 2669; (i) Kawano, Y.; Togo, H. *Tetrahedron* **2009**, *65*, 6251; (j) Ishiwata, Y.; Togo, H. *Tetrahedron Lett.* **2009**, *50*, 5354; (k) Uyanik, M.; Akakura, M.; Ishihara, K. *J. Am. Chem. Soc.* **2009**, *131*, 251; (l) Uyanik, M.; Fukatsu, R.; Ishihara, K. *Org. Lett.* **2009**, *11*, 3470; (m) Ojha, L. R.; Kudugunti, S.; Maddukuri, P. P.; Kommareddy, A.; Gunna, M. R.; Dokuparthi, P.; Gottam, H. B.; Botha, K. K.; Parapati, D. R.; Vinod, T. K. *Synlett* **2009**, 117.
4. Koser, G. F.; Lodaya, J. S.; Ray, D. G., III; Kokil, P. B. *J. Am. Chem. Soc.* **1988**, *110*, 2987.
5. Shah, M.; Taschner, M. J.; Koser, G. F.; Rach, N. L. *Tetrahedron Lett.* **1986**, *27*, 4557.