This article was downloaded by: [Johann Christian Senckenberg] On: 03 September 2014, At: 23:56 Publisher: Taylor & Francis Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry

Publication details, including instructions for authors and subscription information: http://www.tandfonline.com/loi/lsyc20

# A Facile Route to Olefins from Vic-Diols Via Cyclic Sulfates with Triphenylphosphine and lodine

Doo Ok Jang<sup>a</sup>, Yung Hyup Joo<sup>b</sup> & Dae Hyan Cho<sup>a</sup> <sup>a</sup> Department of Chemistry, Yonsei University, Wonju, 222-710, Korea

<sup>b</sup> Pacific Corporation, Pharmaceutical Research Institute , Kyounggi-do, 449-900, Korea Published online: 21 Aug 2006.

To cite this article: Doo Ok Jang , Yung Hyup Joo & Dae Hyan Cho (1997) A Facile Route to Olefins from Vic-Diols Via Cyclic Sulfates with Triphenylphosphine and Iodine, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 27:14, 2379-2386, DOI: <u>10.1080/00397919708004099</u>

To link to this article: http://dx.doi.org/10.1080/00397919708004099

### PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and

are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at http://www.tandfonline.com/page/terms-and-conditions

## A FACILE ROUTE TO OLEFINS FROM VIC-DIOLS VIA CYCLIC SULFATES WITH TRIPHENYLPHOSPHINE AND IODINE

Doo Ok Jang<sup>a\*</sup>, Yung Hyup Joo<sup>b</sup> and Dae Hyan Cho<sup>a</sup>

<sup>a</sup>Department of Chemistry, Yonsei University, Wonju 222-710, Korea <sup>b</sup>Pacific Corporation, Pharmaceutical Research Institute, Kyounggi-do 449-900, Korea

**Abstract:** Treatment of cyclic sulfates of *vic*-diols with triphenylphosphine and iodine offers the corresponding olefins in high yields at room temperature. Both cyclic sulfates of *d*,*l*-hydrobenzoin and *meso*-hydrobenzoin give *trans*-stilbene.

The synthesis of olefins from *vic*-diols is an important process for the modification of natural products and refunctionalization of polyhydroxy compounds. Today, a number of methods to offer olefins from *vic*-diols have been reported.<sup>1</sup> A majority of methods need to introduce activating groups, which are transformed to olefins with proper treatment subsequently. Cyclic thionocarbonates of *vic*-diols are the most well known activating groups which are converted to the corresponding olefins by treatment with trialkyl phosphites,<sup>2</sup> 1,3-dimethyl-2-phenyl-1,3,2-diazaphospholidine,<sup>3</sup> iron pentacarbonyl,<sup>4</sup> Raney nickel,<sup>5</sup>

<sup>\*</sup> To whom correspondence should be addressed

tributyltin hydride,<sup>6</sup> *bis*(1,5-cyclooctadecene) nickel,<sup>7</sup> or Zn and an alkyl iodide.<sup>8</sup> The other examples of activating groups are 1,3-dioxolane derivatives,<sup>9</sup> vicinal dixanthates,<sup>10</sup> disulfonates,<sup>11</sup> cyclic phosphates,<sup>12</sup> and phosphoroamidates.<sup>12</sup> Olefins can also be obtained directly from *vic*-diols by treatment with titanium metals,<sup>13</sup> Me<sub>3</sub>SiCl-NaI,<sup>14</sup> Ph<sub>3</sub>P-I<sub>2</sub>-imidazole,<sup>15</sup> Ph<sub>2</sub>PCl-I<sub>2</sub>-imidazole,<sup>16</sup> PBr<sub>3</sub>-CuBr-Zn,<sup>17</sup> or tungsten reagent.<sup>18</sup> Most recently, cyclic sulfates of *vic*-diols have been used as activating groups for the olefination of *vic*-diols with sodium naphthalenide,<sup>19</sup> phosphines,<sup>20</sup> selenocyanate,<sup>21</sup> or telluride ion.<sup>22</sup> However, these méthods have their own drawbacks; non-stereospecity, high temperature, two-step reaction, and using relatively expensive reagents, respectively.

In this paper, we wish to report that cyclic sulfates of vic-diols can be transformed to the corresponding olefins on treatment with diiodophosphorane generated *in situ* from triphenylphosphine and iodine at room temperature. vic-Diols 1 were easily converted to the cyclic sulfates 2 by treatment with thionyl chloride and RuCl<sub>3</sub>·3H<sub>2</sub>O / NaIO<sub>4</sub> sequentially (Scheme 1).<sup>23</sup>

Reacting the cyclic sulfate of dimethyl *L*-tartrate with triphenylphosphine (2 eq) and iodine (1 eq) in dry  $CH_2Cl_2$  at room temperature resulted in the formation of dimethyl fumarate in 85 % isolated yield (Table 1, entry 1). The reaction generated dimethyl fumarate even with catalytic amount of iodine without affecting the yield of olefin (entry 2 and 3). At the end of the reaction, the brown color of iodine was persistent. These results show that a cyclic sulfate **4** is opened by a diiodophosphorane giving an acyclic sulfate **5**, which can undergo elimination by another diiodophosphorane to generate olefin **6** in stereospecific way, triphenylphosphine oxide, sulfur trioxide, diiodophosphorane, and iodine. Iodine reacts with triphenylphosphine to regenerate diiodophosphorane (Scheme 2, path a). The reaction was not completed with less than 2 eq of Ph<sub>3</sub>P. In blank



Scheme 1

Entry	Cyclic Sulfate (2)		Ph <sub>3</sub> P	l <sub>2</sub>	Time	3
	<u>R1</u>	R <sup>2</sup>	(eq)	(eq)	(hr)	(%) <sup>a</sup>
1	CO <sub>2</sub> CH <sub>3</sub>	CO <sub>2</sub> CH <sub>3</sub>	2	1	2	85
2	CO <sub>2</sub> CH <sub>3</sub>	$CO_2CH_3$	2	0.5	2	85
3	$CO_2CH_3$	CO <sub>2</sub> CH <sub>3</sub>	2	0.1	3	82
4	<i>dl</i> -Ph	Ph	2	1	3	85
5	<i>dl</i> -Ph	$CO_2CH_3$	2.5	1	4	73
6	<i>dl</i> -Ph	CH <sub>2</sub> OCH <sub>3</sub>	2	1	4	73
7	<i>dl-</i> CH <sub>3</sub> (CH <sub>2</sub> ) <sub>4</sub>	CO <sub>2</sub> Bn	3	1	4	93
8	dl-CH <sub>3</sub> (CH <sub>2</sub> ) <sub>9</sub>	н	3	1	5	86

<sup>a</sup>lsolated yields by column chromatography on silica gel.

experiment (without  $Ph_3P$  or  $I_2$ ) the starting cyclic sulfate was recovered. Various cyclic sulfates of *vic*-diols could be converted to the corresponding olefins (entry 4-7). It is worthy of note that cyclic sulfate of inactivated 1,2-dodecandiol was transformed to 1-dodecene under these reaction conditions (entry 8). However, cyclic sulfate of 1,2-cyclododecandiol needed higher temperature (boiling DMF) to

transform to cyclododecene (65 %). Cyclic sulfate of sterically hindered 1,2:5,6di-*O*-isopropylidene-*D*-mannitol was intact under the conditions.



When cyclic sulfate of *meso*-dimethyl tartrate **10a** was treated with  $Ph_3P$  (2 eq) and  $I_2$  (1 eq), dimethyl fumarate **11a** was obtained in 86 % yield exclusively. Similarly cyclic sulfate of *meso*-hydrobenzoin **10b** gave *trans*-stilbene **11b** in 80 % yield. These imply that an acyclic intermediate **7** which is formed from cyclic sulfates of *cis*-diols by nucleophilic attack by an diiodophosphorane may change the conformation to give thermodynamically stable *trans*-olefins (Scheme 2, path b).

In conclusion, we have developed a procedure for the synthesis of olefins from *vic*-diols using triphenylphosphine and iodine at room temperature. Both d,l- and *meso-vic*-diols can be transformed into thermodynamically stable *trans*-olefins under mild conditions.



#### Scheme 3

**Typical experimental procedure:** To a solution of the cyclic sulfate of dimethyl *L*-tartrate (0.24 g, 1 mmol) in dry  $CH_2Cl_2$  (5 mL) under nitrogen was added Ph<sub>3</sub>P (0.52 g, 2 mmol) and I<sub>2</sub> (0.25 g, 1 mmol) at room temperature. The reaction mixture was stirred for 2 hr (TLC showed the disappearance of the cyclic sulfate). The reaction mixture was diluted with  $CH_2Cl_2$  and washed with saturated aqueous Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution until the brown color disappeared. The organic layer was dried over anhydrous MgSO<sub>4</sub>. After filtration, the solvent was removed and the residue was purified with column chromatography on silica gel ( $CH_2Cl_2$  / hexanes, 3:1) to give dimethyl fumarate (0.12 g, 85 %).

### References

 Review of olefin synthesis from vic-diols: a) Block, E. Organic reactions, 1984, 30, 457. b) Larock, R.C., "Comprehensive Organic Transformations," VCH, New York, 1989, pp 155-156. c) Kunz, H. and Waldmann, H. "Comprehensive Organic Synthesis," Trost, B., Ed.; Pergamon, Oxford, 1991, Vol 6, pp 685-688.

- a) Corey, E.J. and Winter, R.A.E. J. Am. Chem. Soc. 1963, 85, 2677.
   b) Corey, E.J., Carey, F.A. and Winter, R.A.E. J. Am. Chem. Soc. 1965, 87, 934.
- a) Corey, E.J. and Hopkins, P.B. Tetrahedron Lett. 1982, 23, 1979. b) Kato, N., Nakanishi, K. and Takeshita, H. Bull. Chem. Soc. Jpn. 1986, 20, 1109. c) Chu, C.K., Bhadti, V.S., Doboszewski, B., Gu, Z.P., Kosugi, Y., Pullaiah, K.C. and Van Roey, P. J. Org. Chem. 1989, 54, 2217. d) Manchand, P.S., Belica, P.S., Holman, M.J., Huang, T-N, Maehr, H., Tam, S.Y-K, Yang, R.T., Partridge, J.J., Petrin, M.J., Pico, A.M., Schnurrman, E.S. and West, R.C. J. Org. Chem. 1992, 57, 3473.
- 4. Daub, J., Trautz, V. and Erhardt, U. Tetrahedron Lett. 1972, 4435.
- Kutney, J.P., Bunzil-Trepp, U., Rohr, M. and Worth, B.R. J. Am. Chem. Soc. 1978, 100, 4220.
- Kutney, J.P., Honda, T., Kazmaier, P.M., Lewis, N.J. and Worth, B.R. *Helv. Chim. Acta* 1980, 63, 366.
- 7. Semmelhack, M.F. and Stauffer, R.D. Tetrahedron Lett. 1973, 2667.
- 8. Vedejs, E. and Wu, E.S.C. J. Org. Chem. 1974, 39, 3641.
- 9. a) Crank, G. and Eastwood, F.W. Aust. J. Chem. 1964, 17, 1392. b) Josan, J.S. and Eastwood, F.W. Aust. J. Chem. 1968, 21, 2013. c) Eastwood, F.W., Harrington, K.J., Josan, J.S. and Pura, J.L. Tetrahedron Lett. 1970, 5223. d) Hanessian, S., Bargiotti, A. and LaRue, M. Tetrahedron Lett. 1978, 737.
- a) Barrett, A.G.M., Barton, D.H.R., Bielski, R. and McCombie, S.W. J. Chem. Soc., Chem. Commun. 1977, 866. b) Barrett, A.G.M., Barton,

D.H.R. and Bielski, R. J. Chem. Soc., Perkin Trans. I 1979, 2378. c)
Barton, D.H.R., Jang, D.O. and Jaszberenyi, J.Cs. Tetrahedron Lett.
1991, 32, 2569. d) Barton, D.H.R., Jang, D.O. and Jaszberenyi, J.Cs. Tetrahedron Lett. 1991, 32, 7187.

- a) Carnahan, J.C., Jr. and Closson, W.D. Tetrahedron Lett. 1972, 3447.
   b) Hrovat, D.A., Miyake, F., Trammell, G., Gilbert, K.E., Mitchell, J., Clardy, J. and Borden, W.T. J. Am. Chem. Soc. 1987, 109, 5524.
- a) Marshall, J.A. and Lewellyn, M.E. Synth. Commun. 1975, 5, 293. b)
  Marshall, J.A. and Lewellyn, M.E. J. Org. Chem. 1977, 42, 1311. c)
  Marshall, J.A. and Lewellyn, M.E. J. Am. Chem. Soc. 1977, 99, 3508.
- a) McMurry, J.E. and Fleming, M.P. J. Org. Chem. 1976, 41, 896. b)
   McMurry, J.E. Acc. Chem. Res. 1983, 16, 406.
- Sarma, J.C., Barua, N.C., Sharma, R.P. and Barua, J.N. *Tetrahedron* 1983, 39, 2843.
- a) Garegg, P.J. and Samuelsson, B. Synthesis 1979, 469. b) Luzzio,
   F.A. and Menes, M.E. J. Org. Chem. 1994, 59, 7267.
- 16. Liu, Z., Classon, B. and Samuelsson, B. J. Org. Chem. 1990, 55, 4273.
- Tanaka, A., Yasuda, H., Yamamoto, H. and Nozaki, H. J. Am. Chem. Soc. 1975, 97, 3252.
- Sharpless, K.B. and Flood, T.C. J. Chem. Soc., Chem. Commun. 1972, 370.
- a) Nonaka, T., Kihara, S., Fuchigami, T. and Baizer, M.M. Bull. Chem. Soc. Jpn. 1984, 57, 3160. b) Beels, C.M.D., Coleman, M.J. and Taylor, R.J.K. Synlett 1990, 479.
- Kim, K.S., Joo, Y.H., Kim, I.W., Lee, K.R., Cho, D.Y., Kim. M. and Cho, I.H. Synth. Commun. 1994, 24, 1157.

- Santoyo-González, F., Garcia-Calvo-Flores, F., Garcia-Mendoza, P., Hernandez-Mateo, F., Isac-Garcia, J. and Pérez-Alvarez, D.J. J. Chem. Soc., Chem. Commun. 1995, 461.
- 22. Chao, B., McNulty, K.C. and Dittmer, D.C. *Tetrahedron Lett.* **1995**, *36*, 7209.
- 23. a) Gao, Y. and Sharpless, K.B. J. Am. Chem. Soc. 1988, 110, 7538. b)
  Kim, B.M. and Sharpless, K.B. Tetrahedron Lett. 1989, 30, 655.

(Received in Japan 13 December 1996)