

- J. J. *Org. Chem.* **1996**, *61*, 359 and references therein.
4. For recent reviews on the reactions with samarium diiodide, see: (a) Molander, G. A.; Harris, C. R. *Chem. Rev.* **1996**, *96*, 307. (b) Molander, G. A. *Org. React.* **1994**, *46*, 211. (c) Imamoto, T. *Lanthanides in Organic Synthesis*; Academic Press: London, 1994; pp. 23-62. (d) Molander, G. A.; Harris, C. R. *Chem. Rev.* **1992**, *92*, 29.
5. For reviews on the cleavage of isoxazoline N-O bonds,

- see: Curran, D. P. *In Advances in Cycloaddition*; Curran, D. P. Ed.; JAI Press Inc.: London, U. K., 1988; vol 1, pp 129-189.
6. For the preparation of a solution of samarium diiodide in tetrahydrofuran, see: Imamoto, T. *Lanthanides in Organic Synthesis*; Academic Press: London, 1994; p 21.
7. Further work is in progress to locate the origin of lower yield in this case and to improve the yield of **3e**.

## Diastereoselective Routes in the Paterno-Büchi Reaction of Cyclic Enol Ortho Ester with Aldehydes†

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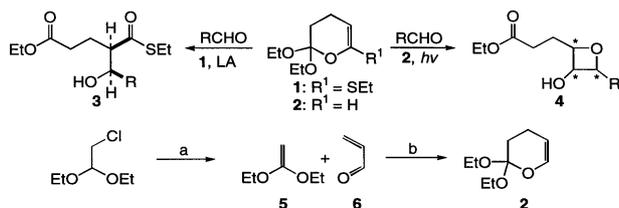
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In confluence with the wide spread advances in synthetic methods, particularly diastereoselective routes, the Paterno-Büchi reaction has prospered and led to significant developments in the area of synthetic organic chemistry.<sup>1</sup> The Paterno-Büchi reaction represented by the [2+2] photocycloaddition of carbonyl functionality to alkene provides a unique way of route to functionalized oxetane.<sup>2</sup> There have been several investigations directed towards diastereoselectivity in this reaction using enol ethers mainly due to the generation of up to three new stereogenic centers during the process.<sup>3</sup> We recently reported the diastereoselective synthesis of highly functionalized aldol products of glutarates **3** from the reaction of dihydropyran **1** with aldehydes promoted by a Lewis acid catalyst.<sup>4</sup> The efficiency of this transformation concerning diastereocontrolled process has encouraged us to apply the extension of this substrate to structurally unique systems. We report herein our discovery of a broadly useful method for assembling products **4** from the photochemical reaction of 2,2-diethoxy-3,4-dihydro-2*H*-pyran (**2**) with aldehydes as depicted in Scheme 1. The method described herein is successful with several aldehydes and affords products with useful levels of diastereoselectivity.

Starting material **2** was prepared in quantity by a two step sequence, purified by distillation, and stable to storage. Treatment of chloroacetaldehyde diethyl acetal with *t*-BuOK in *t*-BuOH afforded ketene acetal **5** in 78% yield after distilla-



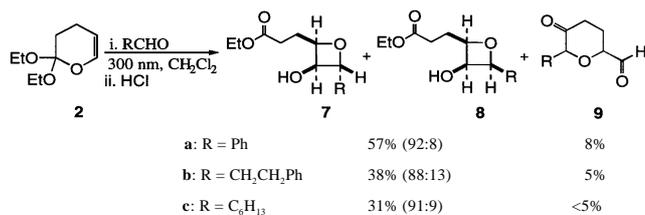
**Scheme 1.** (a) *t*-BuOK, *t*-BuOH, (b) 2,6-Di-*tert*-butylphenol (0.5 mol%), 180 °C, 2 h, sealed tube.

†Dedicated to Prof. Sang Chul Shim on the occasion of his 60th birthday.

tion. The hetero Diels-Alder reaction of **5** with acrolein in the presence of 2,6-di-*tert*-butylphenol (0.5 mol %) at 180 °C for 2h in a sealed tube afforded adduct **7** in 74% yield.<sup>5</sup> The stage was thus set for the photochemical cycloaddition of **2** with aldehydes.

The initial study for orienting experiments focused on the feasibility of substrate **2** for the photochemical cyclization with achiral aldehydes. Preliminary studies on the reaction of **2** with benzaldehyde indicated that the conversion to the corresponding product could be realized by irradiation of the reaction mixture at 300 nm. After surveying numerous conditions, several key findings emerged: (i) optimal chemical yields and diastereo-selectivities were observed with the use of CH<sub>2</sub>Cl<sub>2</sub> as a solvent compared to other solvents such as benzene and acetonitrile; (ii) a 2 : 1 mixture of aldehyde/dihydropyran **2** proved to be the most effective in terms of chemical yield; (iii) benzaldehyde exhibited better reactivity than aliphatic aldehydes; (iv) interesting observation was made that the formation of rearranged product **9** during the photocycloaddition was detected. The photochemical cycloaddition was performed according to the following general procedure: A quartz tube was charged with benzaldehyde Eq. (2) and dihydropyran **2** Eq. (1) dissolved in degassed CH<sub>2</sub>Cl<sub>2</sub>. The sample was irradiated at 300 nm at room temperature for 3 h, and then the irradiation was stopped. After cooled to 0 °C, the reaction mixture was treated with 0.5 N aqueous HCl followed by work up and silica gel chromatography to afford inseparable oxetanes **7a** and **8a** in a ratio of 92 : 8 as judged by <sup>1</sup>H NMR along with the minor product **9a** (3 : 2 diastereomeric mixture). The results obtained with other aldehydes are summarized in Scheme 2.

Although the exact mechanistic aspects of this transformation have not been rigorously elucidated, the following pathway could be a probable chemical and stereochemical routes on the basis of product population. According to the mechanistic studies for photocycloadditions,<sup>6</sup> a putative 1,4-diradical intermediate for the oxetane formation resulted from the addition of n,π\* triplet state of carbonyl compound to



Scheme 2.

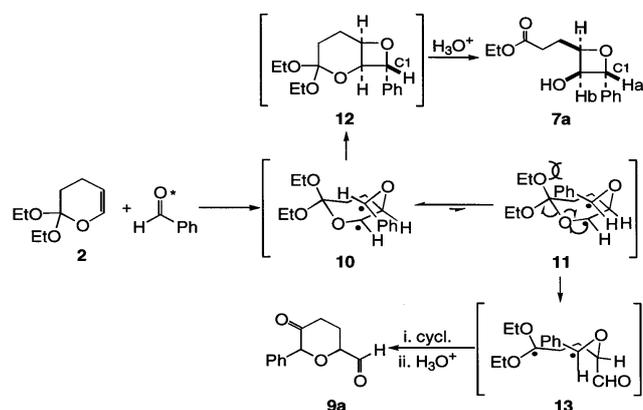


Figure 1. Plausible Reaction Pathways

alkene.<sup>7</sup> The diradical led to the formation of oxetane stereoselectively through more stable radical orientation due to the steric and stereoelectronic factors. Therefore, treatment of dihydro-pyran **2** with the excited benzaldehyde initiated by irradiation resulted in the formation of diradical species as depicted in Figure 1. The observed preference for the relative geometry of diradical species **10** rather than **11** could be rationalized in terms of two possible transformations. Cyclization of **10** led to the formation of somewhat unstable **12**,<sup>8</sup> and subsequent acidic work up provided the major oxetane **7**. The formation of minor product **9** could be explained by the cyclization of the reorganized radical species **13** mainly from the unstable **11**. Since two diastereomers **7** and **8** must be derived from the structurally rigid **12** and its epimer, it follows that **7a** differ from **8a** only in the relative stereochemistry at C1. The stereochemistry of the major component **7** in each case was determined based on the vicinal coupling patterns in the <sup>1</sup>H NMR spectra. The *trans-cis* stereochemical assignments in oxetane are often based on the magnitude of vicinal coupling constants resulting from the optimal conformation.<sup>9</sup> The smaller coupling constant for Ha (doublet,  $J_{HaHb}$ =6.21 Hz at  $\delta$  5.88) obtained from the spectrum of **7a** (R=Ph) clearly indicated *trans* configuration whereas a doublet coupling of 7.88 Hz at  $\delta$  6.12 of minor component **8a** implied it to be *cis*. These mechanistic speculations and <sup>1</sup>H NMR studies clearly indicates that the major components of these transformations have *trans* stereochemi-

cal relationships. These stereochemical outcomes are well consistent with previously reported results.<sup>1,10</sup>

In summary, this paper describes diastereoselective synthesis of highly functionalized oxetanes by means of photocycloaddition of dihydro-pyran **2** and achiral aldehydes in a very general way which promises to be widely applicable. Further studies including synthetic application and extension of this method into enantiomeric pathways are in progress.

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## References

- For an excellent review, see: Porco, J. A. Jr.; Schreiber, S. L. In *Comprehensive Organic Synthesis*; Trost, B. M.; Fleming, I. Eds.; Pergamon Press: Oxford, U.K., 1991; Vol. 5, p 151.
- For general discussions, see: (a) Inoue, Y. *Chem. Rev.* **1992**, *92*, 741. (b) Winkler, J. D.; Bowen, C. M.; Liotta, F. *Chem. Rev.* **1995**, *95*, 2003.
- (a) Bach, T.; Jödicke, K.; Kather, K.; Fröhlich, R. *J. Am. Chem. Soc.* **1997**, *119*, 2437. (b) Bach, T. *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 884. (c) Bach, T.; Jödicke, K.; Kather, K.; Fröhlich, R. *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2271.
- (a) Yu, C.-M.; Choi, H.-S.; Lee, J.-K.; Yoon, S.-K. *J. Org. Chem.* **1997**, *62*, 6687. (b) Yu, C.-M.; Jung, W.-H.; Choi, H.-S.; Lee, J.; Lee, J.-K. *Tetrahedron Lett.* **1995**, *36*, 8255.
- Boeckman, R. K. Jr.; Brunza, K. J. *Tetrahedron* **1981**, *37*, 3997.
- Griesbeck, A. G.; Mauder, H.; Stadtmüller, S. *Acc. Chem. Res.* **1994**, *27*, 70 and also references cited therein.
- (a) Freilich, S. C.; Peters, K. S. *J. Am. Chem. Soc.* **1985**, *107*, 3819. (b) Schuster, D. I.; Heibel, G. E.; Brown, P. B.; Turro, N. J.; Kumar, C. V. *J. Am. Chem. Soc.* **1988**, *110*, 8261.
- We tried to isolate intermediate **12** under various neutral or basic conditions, but unsuccessfully. The major component was always **7** along with several minor components. However, after mild acidic work up, **7** was cleanly obtainable.
- Pretsch, E.; Clerc, T.; Seibl, J.; Simon, W. *Tables of Spectral Data for Structure Determination of Organic Compounds*; Springer-Verlag: Berlin, Germany; 1989; p H65.
- (a) Jones, G.; Acquadro, M. A.; Carmody, M. A. *J. Chem. Soc. Chem. Comm.* **1975**, 206. (b) Schreiber, S. L.; Porco, J. A. Jr. *J. Org. Chem.* **1989**, *54*, 4721. (c) Buhr, S.; Griesbeck, A. G.; Lex, J.; Mattay, J.; Schroer, J. *Tetrahedron Lett.* **1996**, *37*, 1195.