Tetrahedron Letters, Vol. 34, No. 47, pp. 7627-7628, 1993
Printed in Great Britain

0040-4039/93 $6.00 + .00
Pergamon Press Ltd

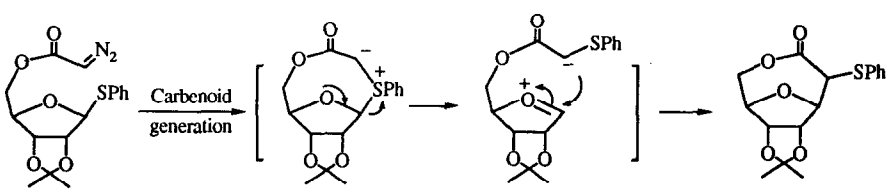
A NOVEL ROUTE TO A NEW LACTONE INTERMEDIATE FOR C-NUCLEOSIDES *VIA* AN INTRAMOLECULAR SULFONIUM YLIDE REARRANGEMENT. A FORMAL SYNTHESIS OF (+)-SHOWDOMYCIN

Guncheol Kim*, Sunwha Kang and Soon Nam Kim

Hanhyo Institutes of Technology, San 6, Daeyadong, Siheungshi, Kyunggido, Korea, 429-010

Abstract: *The lactone of 3,6-anhydro-4,5-O-isopropylidene-2-thiophenoxy-D-allo-heptonic acid was prepared by means of an intramolecular carbenoid-phenylthiofuranose reaction.*

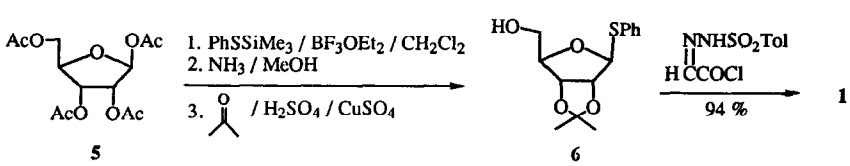
The chemistry of intramolecular sulfonium ylide formation from the reaction of carbenoid with divalent sulfur compound and its rearrangement to the useful structures has been increasingly studied recently.[1,2] In this paper we disclose the preparation of the lactone intermediate **4** *via* the 8-membered cyclic sulfonium ylide **2**, the sequential oxonium intermediate **3** and stereoselective intramolecular β-C-glycosilation (Scheme 1). Intermolecular C-glycosilation of several thioglycosides *via* a carbenoid displacement reaction had been explored in Kamentani's group.[3] However, intramolecular carbenoid reactions to prepare C-glycosides selectively have been rare until recently. In this design the proper diazo-intermediate should be 1-β-phenylthiofuranoside equipped with diazoacetic ester tethered to the primary 5-hydroxy group.



1 **2** **3** **4**

Scheme 1

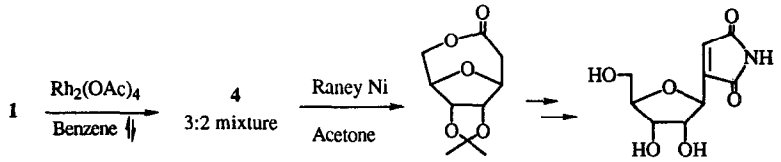
Diazoacetic ester **1** was prepared from β-phenylthio-2,3-O-isopropylidene-D-ribofuranose **6** (94%) by using Corey's modified method.[4] The furanose **6** was readily obtained by three step procedures, the selective



5 **6**

Scheme 2

conversion of the ribofuranose-tetraacetate **5** to 1-β-(phenylthio)-triacetate (97%),[5] the deprotection of acetyl groups by ammonia in MeOH (98%) and the conventional protection[6] to the isopropylidene **6** (83%).



Scheme 3

The desired lactone **4** was formed in a refluxing solution of **1** in benzene (0.1 M) containing 1 mol % of rhodium (II) acetate in 48% yield as a 3:2 mixture of separable epimers.[7] The yield of **4** could be increased to 56% by slow addition of the solution of **1** by means of a syringe pump to a refluxing benzene.[8] Desulfurization of each isomer of **4** by Raney Ni in acetone converted them to **7** (75% respectively), which is identical with the known compound,[9] m.p. 163 - 164 °C {lit.[10] m.p. 161-163 °C}; $[\alpha]_D^{24}$: + 83.4 (c 0.63, $CHCl_3$) {lit.[10] $[\alpha]_D^{24}$: + 84 (c 0.63, $CHCl_3$)}.

Since the lactone **4** could be easily converted to **7**, the key intermediate for several C-nucleosides[10,11] including showdomycin, further application of the compound **4** to C-nucleosides is under investigation.

References and Notes

1. a) Moody, C. J.; Taylor, R. J. *Tetrahedron* **1990**, *46*, 6501. b) Kurdth, M. J.; Tahir, S. H.; Olmstead, M. M. *J. Org. Chem.* **1990**, *55*, 2286. c) Dowis, H. M. L.; Crisco, L. van T. *Tetrahedron Lett.* **1987**, *28*, 371. d) Kametani, T.; Yukawa, H.; Honda, T. *J. Chem. Soc., Chem. Comm.* **1986**, 651.
2. Reviews on the ylide generation from carbenes and carbenoids with heteroatoms. a) Adams, J.; Spero, D. M. *Tetrahedron* **1991**, *47*, 1765. b) Padwa, A. ; Hornbuckle, S. F. *Chem. Rev.* **1991**, 91, 263. c) Ando, W. *Acc. Chem. Res.* **1977**, *10*, 179.
3. Kametani, T; Kawamura, K.; Honda, T. *J. Am. Chem. Soc.* **1987**, *109*, 3010.
4. Corey, E. J.; Myers A. G. *Tetrahedron Lett.* **1984**, *33*, 3559.
5. Nambiar, S; Daeuble, J. F.; Doyle R. J.; Taylor, K. G. *Tetrahedron Lett.* **1989**, *30*, 2179.
6. Levene P. A.; Stiller E. T. *J. Biol. Chem.* **1933**, *102*, 187.
7. For major isomer of **4**; ^{1}H NMR (300 MHz C_6D_6): δ= 1.02 (s, 3H); 1.45 (s, 3H); 3.25 (dd, J= 3.8 Hz, 13.7 Hz, 1H); 3.57 (d, J= 13.8 Hz, 1H); 4.00 (d, J=3.7 Hz, 1H); 4.18 (d, J= 1.8 Hz, 1H); 4.56 (d, J= 1.7 Hz, 1H); 4.69 (d, J= 5.7 Hz, 1H); 4.87 (d, J= 5.7 Hz, 1H); 6.90 (m, 3H); 7.45 ppm (dd, J= 1.9 Hz, 5.8 Hz, 3H): ^{13}C NMR (75 MHz, C_6D_6): δ= 24.3; 26.3; 57.6; 71.3; 81.9; 82.9; 83.4; 83.5; 129.6; 128.1; 129.8; 132.7; 133.3 ppm.
8. The other products were 1:1 mixture of cis and trans self-coupled dimers(8%).
9. For **7**: ^{1}H NMR (300 MHz C_6D_6): δ= 1.08 (s, 3H); 1.47 (s, 3H); 2.18 (dd, J= 2.1 Hz, 16.2 Hz, 1H); 2.46 (dd, J= 5.2 Hz, J= 16.2 Hz, 1H); 3.28 (dd, J=4.0 Hz, J=13.8 Hz, 1H); 3.48 (d, J= 13.8 Hz, 1H); 3.98 (m, 2H); 4.52 (d, J= 5.7 Hz, 1H); 4.71 ppm (d, J= 5.7 Hz, 1H).
10. Sato, T.; Hayakawa, Y.; Noyori, R. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 2515.
11. Noyori, R.; Sato, T.; Hayakawa, Y. *J. Am. Chem. Soc.* **1978**, *100*, 2561.

(Received in Japan 19 July 1993)