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HIGHLY PERISELECTIVE [2,3]WITTIG REARRANGEMENTS ON DIHYDROFURAN AND DIHYDROPYRAN RINGS

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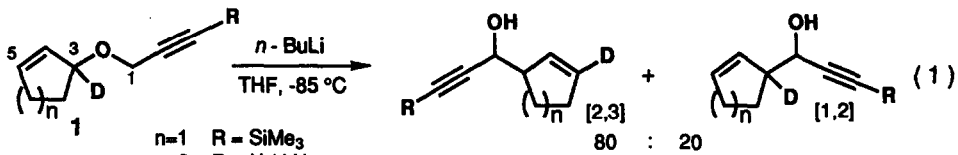
Summary: The carbanion {3,5}-rearrangements involving the dihydrofuran and dihydropyran rings as migrating groups are shown to afford exclusively the [2,3]Wittig products with a remarkably high periselectivity and stereoselectivity.

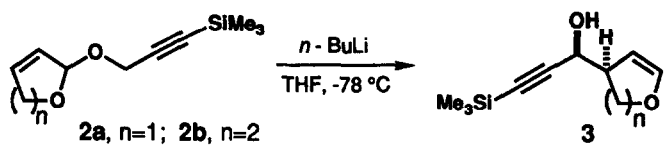
The [2,3]Wittig rearrangement of acyclic allyl ether systems are widely used in stereoselective synthesis.[1] In the rearrangements of certain types of cyclic substrates, however, a serious regiochemical problem arises in terms of the competitive [2,3]- *vs.* [1,2]-shift.[1] For instance, the {3,5}-rearrangement[2] of type **1** yields a mixture of the [2,3]- and [1,2]-products (eq 1).[3]



(1)

n=1 R = $SiMe_3$ 80 : 20
n=2 R = H (Li) 38 : 62

We now report that the {3,5}-rearrangement of the dihydrofuran and pyran systems **2** proceeds exclusively in a [2,3]sigmatropic fashion to afford only the [2,3]Wittig product **3** with a high stereoselectivity (eq 2).

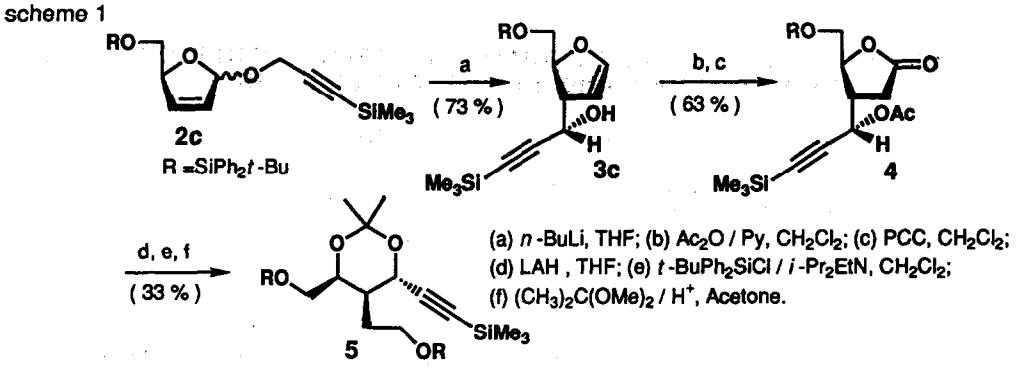


2a, n=1; **2b**, n=2 **3**

(2)

The substrates **2a** and **2b** were prepared in 75-80 % yield from the corresponding lactols[4] *via* glycosidation with the γ-silylpropargyl alcohol in the presence of a catalytic amount of *p*-toluenesulfonic acid. The rearrangement of dihydrofuran **2a** was carried out under the standard conditions (*n*-BuLi, THF, -78 °C) to afford 64 % yield of the [2,3]Wittig product **3a** as a single stereoisomer.[5,6] Any trace of the [1,2]-product was not detected by NMR analysis. Likewise, dihydropyran **2b** afforded 67 % yield of the [2,3]-shifted product **3b** exclusively.[6,7] Particularly notable are the remarkably high periselectivity, indicating that the oxacyclic system is better suited for the [2,3]Wittig shift compared with the carbocyclic counterpart. To gain an insight about diastereofacial selectivity in the rearrangement, we performed the reaction of dihydrofuran system **2c** (α / β = 85 / 15)[8] which was prepared in 78 % yield from the lactol derived from the (*S*)-5-siloxymethyl-2(5H)-furanone[9] as described above. We found that the carbanion rearrangement of **2c** afford exclusively the [2,3]Wittig product **3c** with a high peri- and diastereoselectivity.[10] The stereochemistry of **3c** was assigned through the ^1H NMR analysis including NOE experiments of cyclic acetal **5**[11] which was derived *via* the lactone **4**[12] as depicted in scheme 1. The assigned stereochemistry of **3c** reveals that the rearrangement occurs exclusively on the less hindered α-face[13] to establish the erythro configuration on the side chain.

scheme 1



In conclusion, we have now presented the first examples of the {3,5}-[2,3]Wittig variants in which the allylic array is incorporated in a ring system. Synthetic application of the present type of cyclic [2,3]Wittig rearrangement is now in progress.

Acknowledgment

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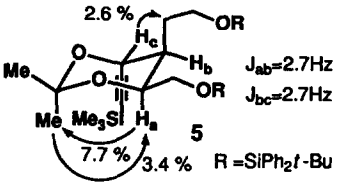
References and Notes

(1) For a review on [2,3]Wittig rearrangement, see: T. Nakai and K. Mikami, *Chem. Rev.*, **86**, 885 (1986).
(2) For the terminology of "{m,n}-rearrangement", see: F. E. Ziegler, *Chem. Rev.*, **88**, 1423 (1988).
(3) Unpublished results from our laboratory. Also see: N. Sayo, Y. Kimura, and T. Nakai, *Tetrahedron Lett.*, **23**, 3931 (1982).
(4) The lactols were prepared from the lactones *via* reduction with DIBAL in toluene at -78 °C.
(5) **3a**: ^{1}H NMR (200 MHz, $CDCl_3$), δ 4.18 (dd, J=7.0 and 4.8 Hz, 1H, C*H*(OH)), 4.91 (dd, J=2.6 and 2.6 Hz, 1H, OCH=C*H*), 6.43 (dd, J=2.6 and 2.6 Hz, 1H, OC*H*=CH); ^{13}C NMR (50 MHz, $CDCl_3$), δ -0.44, 49.55, 64.86, 71.70, 90.48, 99.66, 105.01, 148.48.
(6) The relative stereochemistry of **3a** and **3b** has not been determined yet. However, the erythro configuration is strongly suggested by the consideration of the transition state model (ref 1), coupled with the NMR similarity to that of **3c** (*vida infra*).
(7) **3b**: ^{1}H NMR ($CDCl_3$), δ 4.13 (d, J=7.2 Hz, 1H, C*H*(OH)), 4.69 (dd, J=6.4 and 3.2 Hz, 1H, OCH=C*H*), 6.47 (dd, J=6.4 and 2.0 Hz, 1H, OC*H*=CH); ^{13}C NMR ($CDCl_3$), δ -0.44, 24.68, 36.87, 64.05, 66.05, 90.50, 100.47, 105.32, 145.96.
(8) The α / β ratio was determined by ^{1}H NMR assay ($CDCl_3$): the chemical shift due to the 5-hydrogen appears at δ 4.75 - 4.90 (m) for the α-isomer and 4.6 - 4.7 (m) for the β-isomer.
(9) S. Takano, A. Kurotaki, M. Takahashi, and K. Ogasawara, *Synthesis*, **1986**, 403 .
(10) **3c**: ^{1}H NMR (C_6D_6), δ 3.05 - 3.15 (m, 1H, C*H*CH=CH), 4.06 (d, J=7.2 Hz, 1H, C*H*(OH)), 4.65 - 4.75 (m, 1H, OC*H*), 4.77 (dd, J=2.6 and 2.6 Hz, 1H, OCH=C*H*), 6.21 (dd, J=2.6 and 2.6 Hz, 1H, OC*H*=CH); ^{13}C NMR (C_6D_6), δ 0.01, 19.69, 27.17, 52.46, 65.59, 66.96, 84.75, 90.10, 99.99, 106.94, 148.37.
(11) The stereochemistry of **5** was assigned on the basis of the magnitudes of J_{ab} and J_{bc} and the NOE results as shown.



(12) **4**: ^{1}H NMR ($CDCl_3$), δ 5.43 (d, J=4.4Hz, 1H, C*H*(OAc)C≡C); ^{13}C NMR ($CDCl_3$), δ -0.72, 18.96, 20.66, 26.56, 31.19, 40.31, 64.91, 65.09, 81.03, 93.21, 98.94, 169.82, 176.08.
(13) The β-isomer of **2c** was not recovered, suggesting that it would decompose during the reaction.

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