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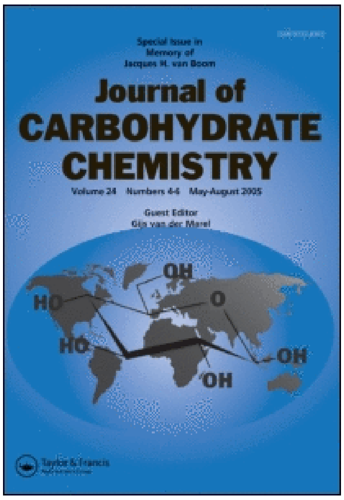

Journal of Carbohydrate Chemistry
Publication details, including instructions for authors and subscription information:
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Communication: Double Bond Migration of a 1,5-Anhydro-3-*C*-*p*-Tolylsulfonyl-D-Hex-2-Enitol Derivative and the Corresponding 5a-Carba-Dl-Sulfonyl Sugar

Tohru Sakakibara; Miwa Shindo; Shinya Narumi; Chihiro Nagano; Yasuhiro Kajihara

To cite this Article Sakakibara, Tohru , Shindo, Miwa , Narumi, Shinya , Nagano, Chihiro and Kajihara, Yasuhiro(2000) 'Communication: Double Bond Migration of a 1,5-Anhydro-3-*C*-*p*-Tolylsulfonyl-D-Hex-2-Enitol Derivative and the Corresponding 5a-Carba-Dl-Sulfonyl Sugar', Journal of Carbohydrate Chemistry, 19: 6, 783 — 788

To link to this Article: DOI: 10.1080/07328300008544116

URL: http://dx.doi.org/10.1080/07328300008544116

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J. CARBOHYDRATE CHEMISTRY, 19(6), 783–788 (2000)

COMMUNICATION

DOUBLE BOND MIGRATION OF A 1,5-ANHYDRO-3-*C*-*p*-TOLYLSULFONYL-D-HEX-2-ENITOL DERIVATIVE AND THE CORRESPONDING 5a-CARBA-DL-SULFONYL SUGAR

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Received September 17, 1999 - Final Form March 21, 2000

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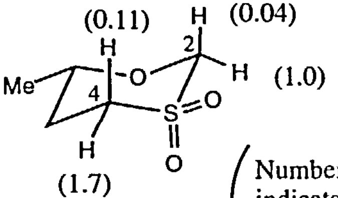
Although the rate of proton abstraction (kinetic acidity) frequently plays an essential role in determination of reaction pathways and is of theoretical interest,[1] it is still controversial whether an oxygen atom activates or deactivates the abstraction of an α-hydrogen atom of an ether. For example, it is well known that oxidative elimination of a seleno group gives an allyl ether as the major product, indicating the oxygen atom deactivates the kinetic acidity.[2] Abstraction of the equatorial hydrogen atom at C-2 of



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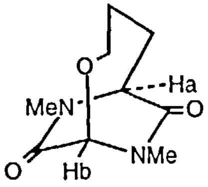
(Numbers in parentheses indicate the relative rates for deuteration.)



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6-methyl-1,3-oxathiane-3,3-dioxide 1 is slower than that at C-4.[3] On the other hand, the bridgehead hydrogen atom (H_b) adjacent to the oxygen atom of piperazinedione (2) is abstracted more readily than that of the alternative one (H_a).[4]

We have reported that the double bond migration of 3-*C*-nitrohex-2-enitol **3** occurred more smoothly than that of the corresponding 5a-carba sugar **6**.[5] On the basis of these results we achieved an unprecedented example, in which a vinyl ether (glycal) became a major product by oxidative elimination of the seleno group of **7**.[5] If these results have generality, the double bond migration of 2-enitol derivatives having an electron-withdrawing group at C-3 should also proceed more smoothly than the corresponding 5a-carba sugar.

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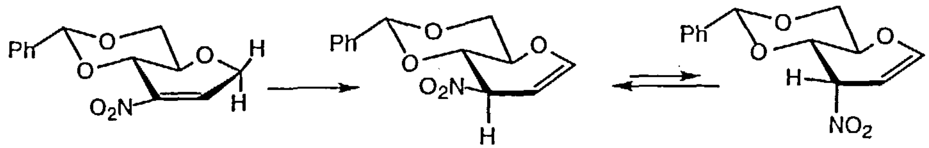
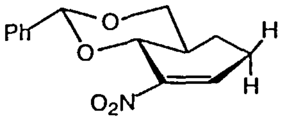


3 **4** **5**



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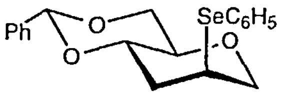

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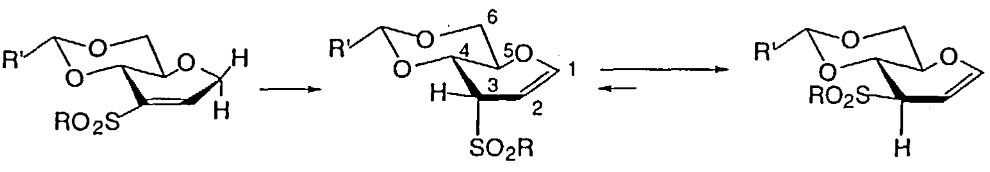
We now report the double bond migration of 1,5-anhydro-3-*C*-*p*-tolylsulfonyl-D-hex-2-enitol **8** and the corresponding 5a-carba-DL-sulfonyl sugar **13**. Furthermore, we examined by *ab initio* calculation whether the thermodynamic stability of the glycal derivatives thus prepared is corroborated or not.

Double bond migration of sulfonyl sugar **8**[6] occurred slowly by treatment with Et_3N in $CDCl_3$. The ratio of starting material **8** to D-allal **9** became 15 : 1, 2.0 : 1, and 0 : 1 after 3, 23, and 30 days, respectively. Under these conditions, there was no evidence



8 R =Tol,R'=Ph

9 R =Tol, R'=Ph
10 R =Me, R'=H

11 R =Tol, R'=Ph
12 R =Me, R'=H

for formation of the alternative 3-epimer (D-glucal **11**), suggesting that **9** was the kinetically controlled product.

Similar treatment of 5a-carba sugar **13**[7] in the presence of excess (x16) Et_3N for 14 days resulted only in the recovery of unreacted **13**. However, when compound **13** was treated with Et_3N in DMSO-d_6 for 13 days, a 5.6 : 1 : 1.2 mixture of starting material **13**, DL-allal **14**, and DL-glucal **16** was obtained. Under the same conditions, **8** gave a 1.2 : 1 mixture of D-allal **9** and D-glucal **11**. These results showed that the double bond migration of **8** occurred more easily than that of **13**. Treatment of **8** with DBU in DMSO-d_6 for 2 h afforded a 1 : 8.4 equilibrium mixture of **9** and **11**; the equilibrium was confirmed by the use of **9** and **11**, respectively, as starting material under the same conditions. When compound **13** was treated with DBU in $CDCl_3$ for 1 day, a 1 : 1 mixture of DL-deoxyallal **14** and DL-deoxyglucal **16** was obtained. Under the same conditions, compounds **14** and **16** were completely recovered. However, when the reaction time was prolonged to 25 days the DL-deoxyglucal **16** was formed as the sole product. These results suggested that **14** was the kinetically controlled product and **16** the thermodynamically controlled product for the reaction. Regardless of these reaction conditions, the double bond migration should proceed by abstraction of an anomeric proton, followed by protonation at C-3.

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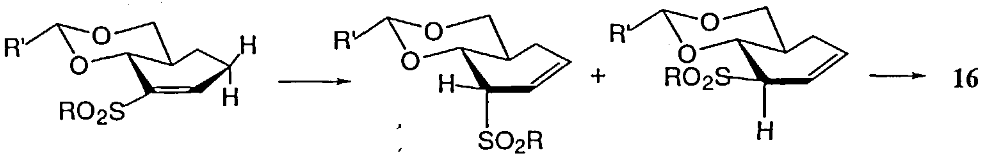

13 R =Tol,R'=Ph

14 R =Tol, R'=Ph
15 R =Me, R'=H

16 R =Tol, R'=Ph
17 R =Me, R'=H

We performed 6-31G* level calculations[8] using model compounds (**10** vs. **12** and **15** vs. **17**) to determine if the calculations could corroborate the experimental results. Different from a planar nitro group, a pyramidal sulfonyl group has many conformers, from which three gauche conformers were calculated for 3-*C*-sulfonyl-D-allal **10** and D-glucal **12**. The most stable conformers were further calculated by including solvent via the Onsager reaction model (ε=4.81, corresponding to the dielectric constant of $CHCl_3$).

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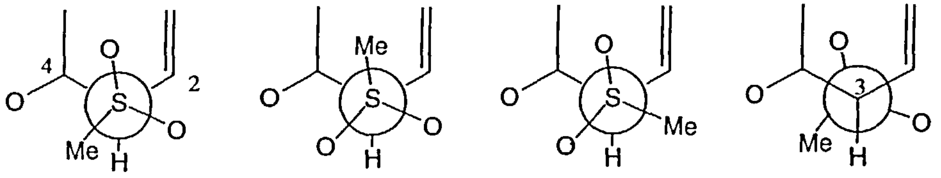


A (0 kJ/mol) B (17.1 kJ/mol) C (20.6 kJ/mol) D

Figure 1. Newman projection of conformers calculated for **12** (value in parentheses shows relative stability in vacuo: the smaller the more stable) and the most stable conformer for **10** (D).

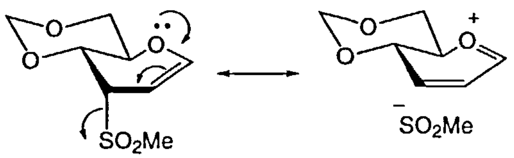
Table 1. Heat of formation (HF), bond length (sugar numbering), dihedral angle, and NBO analysis of methylsulfonyl compounds calculated by 6-31G* with full optimization including solvent via the Onsager reaction model (ε=4.81)

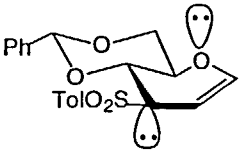
Comp	HF (Hartree)	Bond length (Å) O5-C1	C1-C2	C2-C3	Dihedral angle ∠MeSC3C2	π-$\sigma^*_{C\text{-}S}$ kJ/mol (n_{O5}-$\pi^*_{C=C}$)
10	-1081.6443807	1.344	1.323	1.508	-167°	28.1 (182.6)
12	-1081.6459875	1.348	1.321	1.511	-164°	16.0 (164.1)
15	-1045.8300841		1.321	1.521	-166°	25.2
17	-1045.8326001		1.320	1.514	-162°	13.8

The conformer A was found to be the most stable (Fig. 1), probably due to the absence of electrostatic repulsion between an oxygen atom of the sulfonyl group and the oxygen atom at C-4. Assuming that the ring oxygen atom has no effect on the conformational preference of the sulfonyl group, we employed the most stable conformer obtained in the corresponding sulfonyl sugars as input data for 5a-carba sugars **15** and **17**.

The D-glucal **11** was more stable than the D-allal **9** by 5.3 kJ/mol from the experiment (25 °C) and by 4.2 kJ/mol from *ab initio* calculation of model compounds **12** and **10**. Although the energy difference between the 5a-carba sugars **14** and **16** could not be determined, because the DL-deoxyallal **14** could not be detected by ^{1}H NMR spectroscopy under the thermodynamically controlled conditions, the deoxyglucal **17** was more favorable than the deoxyallal **15** by 6.6 kJ/mol using *ab initio* calculations. Thus relative stabilities calculated are in good agreement with the experimental results.

The lone pair on the ring oxygen atom (O-5) delocalized to the $\sigma^*_{C\text{-}S}$ bond via the double bond as judged from bond length and donor-acceptor values (Table.1); for example, O5-C1, C1-C2, and C2-C3 bond length of **10** is slightly shorter, longer, shorter than the corresponding ones of **12**. However, this delocalization is less effective than with the nitro sugar; for example, donor acceptor stabilization[9] between $\pi_{C=C}$ and $\sigma^*_{C\text{-}S}$ is 28.1 kJ/mol for the allal **10**, while that between $\pi_{C=C}$ and $\sigma^*_{C\text{-}N}$ is 49.8 kJ/mol for the corresponding 3-*C*- nitroallal.[10]





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It was noteworthy that the double bond migration of 3-*C*-nitro-2-enitol **3** gave the D-glucal **4** as a preliminary product, which then epimerized to afford a 2.5 : 1 equilibrium mixture of D-glucal **4** and D-allal **5**.[11] However, in the corresponding sulfonyl sugar **8** the D-allal **9** was first formed, and then epimerized to give a 1 : 8.4 equilibrium mixture of the D-allal **9** and the D-glucal **11**. A conventional carbanion having an electron withdrawing group such as a carbonyl group at the α- position has a planar structure, while the stabilities of the planar and pyramidal structures of α-sulfonylcarbanion are almost the same.[12] Although *ab initio* calculation has not yet succeeded in reproducing the experimental results, it is likely that destabilization between the lone pair on the ring oxygen atom (O-5) and an intermediary α-sulfonylcarbanion makes the *arabino* configuration (the anion occupies the quasiaxial position) less stable, owing to more effective overlap of the molecular orbitals occupying these electrons, than the *ribo* one to afford the D-allal **9** as the preliminary product. If this is the case, the ratio of DL-allal **14** to DL-glucal **16** should be decreased in the 5a-carba sugar **13**, because such destabilization is absent in the 5a-carba sugar. In fact **13** gave a 1 : 1 mixture of **14** and **16** under kinetically controlled conditions, as had been mentioned already.

In conclusion the double bond migration of sulfonyl sugar **8** expectedly proceeded more smoothly than that of 5a-carba sugar **13**. *Ab initio* calculations of model compounds (**10** vs. **12** and **15** vs. **17**) reproduced the relative thermodynamic stabilities.

The D-allal **9** was the kinetic product formed from the sulfonyl sugar **8**, whereas the D-glucal **4** was the product from the nitro sugar **3**.

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