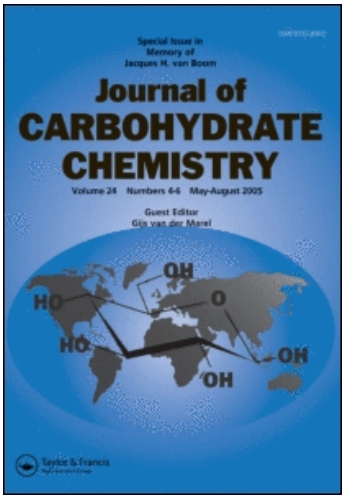

Journal of Carbohydrate Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713617200

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To cite this Article Kim, Kwan Soo , Ahn, Yeong Hee , Park, Suk Bong , Cho, In Haeng , Joo, Yung Hyup and Youn, Byoung Hee(1991) 'Communication: Stereoselective Addition of Phenylsulfonylmethides and Methylmagnesium Halides to Pentodialdo-1,4-Furanoses', Journal of Carbohydrate Chemistry, 10: 5, 911 — 915

To link to this Article: DOI: 10.1080/07328309108543959

URL: http://dx.doi.org/10.1080/07328309108543959

J. CARBOHYDRATE CHEMISTRY, 10(5), 911-915 (1991)

COMMUNICATION

STEREOSELECTIVE ADDITION OF PHENYLSULFONYLMETHIDES AND METHYLMAGNESIUM HALIDES TO PENTODIALDO-1,4-FURANOSES

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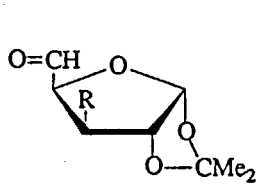
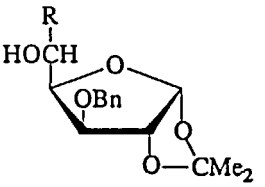
Received September 18, 1990 - Final Form April 19, 1991

Additions of organometallics to chiral α-alkoxy and α,β-dialkoxy carbonyl compounds have recently attracted a great deal of attention since this methodology has a great potential for the synthesis of a variety of polyoxy natural products such as macrolide antibiotics and polyether ionophores. Interpretation of the stereochemical outcome of the addition of organometallics to α,β-dialkoxy carbonyls, however, is rather complex and inconclusive[1] compared to that of α-alkoxy carbonyls.[2]

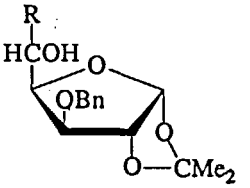
The present communication reports the stereoselective addition of organometallics to two pentodialdo-1,4-furanoses, **1** and **2** which represent an α,β-dialkoxyaldehyde and an α-alkoxyaldehyde, respectively. Additions of organometallics to compound **1** have been reported by Hanessian,[3] Inch,[4] and Danishefsky.[5] We have also reported our own result that the counter cations are the major factor for affecting the stereochemistry at C-5 in the addition of phenylsulfonylmethides to compound **1**.[6] In the continuation of our work, we



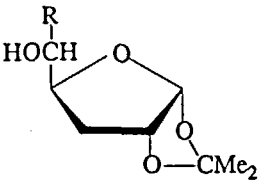
1 R = OBn
2 R = H



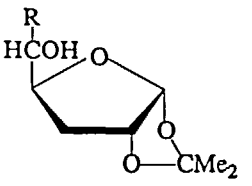
3 R = CH_2SO_2Ph
7 R = CH_3
11 R = CH_2OTs
12 R = CH_2SPh



4 R = CH_2SO_2Ph
8 R = CH_3



5 R = CH_2SO_2Ph
9 R = CH_3
13 R = CH_2OTs
14 R = CH_2SPh



6 R = CH_2SO_2Ph
10 R = CH_3

have further investigated the addition of phenylsulfonylmethides and methylmagnesium halides to pentodialdo-1,4-furanoses, **1** and **2** under various conditions.

The results are summarized in Tables 1-4. Each addition reaction produced a pair of *anti* and *syn* epimers.[7] The stereochemistry at C-5 of the adduct **3-10** was established by the synthesis of the authentic sample[8] of *anti* products through a stereochemically unambiguous synthetic route. Thus, authentic samples of **3** and **5** were prepared by the substitution of the tosyloxy group of **11** and **13** by thiophenoxide and subsequent oxidation

TABLE 1. Addition of $M^{+-}CH_2SO_2Ph$ to Compound **1**

Entry	M	Solvent	Additive	Temp.,℃	Yield,%	Ratio,3/4
1	Li	THF		-78	89	73/27
2	Li	THF		-40	80	68/32
3	Li	THF		0	91	73/27
4	Li	Et_2O		-78	86	71/29
5	Li	THF	HMPA	-78	92	63/37
6	Li	THF	TMEDA	-78	90	70/30
7	Li	THF	$ZnCl_2$	-78	88	67/33
8	Li	THF	$ZnCl_2$/HMPA	-78	92	23/77
9	MgBr	THF		-78	85	95/5

TABLE 2. Addition of $M^{+-}CH_2SO_2Ph$ to Compound **2**

Entry	M	Solvent	Additive	Temp.,℃	Yield,%	Ratio,5/6
1	Li	THF		-78	91	60/40
2	Li	THF	HMPA	-78	90	64/36
3	Li	THF	$MgBr_2$	-78	85	63/37
4	Li	THF	$ZnCl_2$	-78	82	59/41
5	Li	THF	$ZnCl_2$/HMPA	-78	30	17/83
6	MgBr	THF		-78	78	50/50

of the resulting sulfides 12 and 14 with SeO_2-H_2O_2,[6,9] respectively. And authentic samples of 7 and 8 were obtained by the reduction of compounds 11 and 13 with $LiAlH_4$, respectively.

The present results indicate that the counter cation of the nucleophile strongly influences the outcome of the stereochemistry of the addition. As shown in Table 1, when the counter cation is magnesium, *anti* product 3 is highly favored over *syn* product 4 (entry 9) compared to lithium counter cation (entry 1). Therefore, it can be naturally assumed that Mg^{2+} favors β-chelation compared to Li^+. In the addition of phenylsulfonylmethide to compound 2 as shown in Table 2, however, Mg^{2+} afforded a mixture of 5 and 6 in an equal amounts (entry 6), while Li^+ gave *anti* product 5 as the major isomer (entry 1). This result implies that Mg^{2+} chelates β-alkoxy oxygen more strongly than α-alkoxy oxygen, yet the α-chelation of Mg^{2+} is stronger than that of Li^+.

A remarkable result was obtained with zinc as the counter cation. Thus, when $LiCH_2SO_2Ph$, after treatment with HMPA and then with $ZnCl_2$, was added to compound 1 and 2, the ratio of *syn* products increased dramatically (entry 8 in Table 1 and entry 5 in

TABLE 3. Addition of CH_3MgX to Compound 1

Entry	X	Solvent	Additive	Temp.,℃	Yield,%	Ratio,7/8
1	Br	THF		-78	68	54/46
2	Br	Et_2O		-78	74	57/43
3	Br	Et_2O		r.t.	68	37/63
4	I	Et_2O		r.t.	80	35/65
5	Br	Et_2O		reflux	72	30/70
6	Br	Et_2O	$ZnCl_2$	r.t.	75	23/77
7	I	Et_2O	$ZnCl_2$	r.t.	86	12/88
8	Br	Et_2O	$TiCl_4$	-78	68	18/82
9	I	Et_2O	$TiCl_4$	-78	75	7/93

TABLE 4. Addition of CH_3MgBr to Compound 2

Entry	Solvent	Additive	Temp.,℃	Yield,%	Ratio,9/10
1	Et_2O		-78	65	50/50
2	Et_2O		r.t.	80	35/65
3	Et_2O	$ZnCl_2$	r.t.	86	12//88
4	Et_2O	$TiCl_4$	-78	75	7/93

Table 2) compared to the addition in the absence of either HMPA or $ZnCl_2$. This result suggests that Zn^{2+} strongly favors α-chelation. Yet a substantial amount of *anti* products appears to be generated via a nonchelating Felkin model regardless of the counter cations since the addition to compound 2 containing no β-alkoxy group still affords more *anti* products than *syn* products as shown in Table 2.

A similar addition pattern is shown on addition of CH_3MgX to compounds 1 and 2 though the ratio of *syn* products increased slightly compared to the addition of phenylsulfonylmethide. It was found that titanium is an even better α-chelating counter cation than zinc providing *syn* products in high yields as shown in Tables 3 and 4. It is also noteworthy that the proportion of *syn* product 8 increased substantially with increasing reaction temperature and that CH_3MgI afforded a little more *syn* product than CH_3MgBr.

ACKNOWLEDGEMENT

We are grateful to Yonsei University for support of this work.

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1. For example, see : (a) K. Suzuki, Y. Yuki, and T. Mukaiyama, *Chem. Lett.*, 1529 (1981); (b) J. Mulzer and A. Angermann, *Tetrahedron Lett.*, 24, 2843 (1983); (c) K. Mead and T. L. MacDonald, *J. Org. Chem.*, 50, 422 (1985); D. R. Williams and F. D. Klingler, *Tetrahedron Lett.*, 28, 869 (1987).

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6. K. S. Kim, J. K. Sohng, S. B. Ha, C. S. Cheong, D. I. Chung, and C. S. Hahn, *Tetrahedron Lett.*, 29, 2847 (1988).

7. Yields and the ratio of epimers were determined by HPLC analyses. HPLC analyses were performed on Waters Associates μ-Bondapak C_{18} reverse phase columns by employing UV detectors. Epimers 9 and 10 were converted to UV active benzoate forms for the purpose of HPLC analyses.

8. Compounds 3 and 4 : see reference 6.
Compound 5 : TLC (SiO_2, 4:6 hexane/ethyl acetate) R_f = 0.30 ; mp 114 ℃ ; IR (neat) 3400, 1370, 1150 cm^{-1} ; ^1H NMR ($CDCl_3$) δ 1.30 (s, 1H), 1.47 (s, 3H), 1.66 - 2.44 (m, 2H), 2.83 - 3.70 (m, 3H), 3.90 - 4.50 (m, 2H), 4.75 (t, 1H), 5.76 (d, J = 3.5 Hz, 1H), 7.56 - 8.16 (m, 5H).

Compound 6 : TLC (SiO_2, 4:6 hexane/ethyl acetate) R_f = 0.27 ; IR (neat) 3400, 1360, 1150 cm^{-1} ; ^1H NMR ($CDCl_3$) δ 1.30 (s, 3H), 1.47 (s, 3H), 1.73 - 2.27 (m, 2H), 3.25 - 3.58 (m, 3H), 3.92 - 4.42 (m, 2H), 4.65 - 4.93 (m, 1H), 5.80 (d, J = 3.5 Hz, 1H), 7.53 - 8.10 (m, 5H).
Compound 7 and 8 : see reference 4.
Benzoate of compound 9 : TLC (SiO_2, 8:2:3 hexane/ethyl acetate/chloroform) R_f = 0.31 ; mp 86 - 87 ℃ ; ^1H NMR ($CDCl_3$) δ 1.32 (s, 3H), 1.39 (d, J = 5.6 Hz, 3H), 1.54 (s, 3H), 1.62 - 2.32 (m, 2H), 4.25 - 4.45 (m, 1H), 4.73 (t, 1H), 5.07 - 5.38 (m, 1H), 5.85 (d, J = 3.7 Hz, 1H), 7.40 - 7.56 (m, 3H), 7.99 - 8.11 (m, 2H).
Benzoate of compound 10 : TLC (SiO_2, 8:2:3 hexane/ethyl acetate/chloroform) R_f = 0.40 ; mp 63 - 64 ℃ ; ^1H NMR ($CDCl_3$) δ 1.32 (s, 3H), 1.38 (d, J = 6.4 Hz, 3H), 1.53 (s, 3H), 1.62 - 2.32 (m, 2H), 4.20 - 4.46 (m, 1H), 4.75 (t, 1H), 5.20 - 5.35 (m, 1H), 5.82 (d, J = 3.6 Hz, 1H).
All new compounds gave satisfactory microanalytical and spectral data.

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