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Diastereoselective Synthesis of 2,6-Imino-D-allonates from Chromium Carbene Iminosugars[1]

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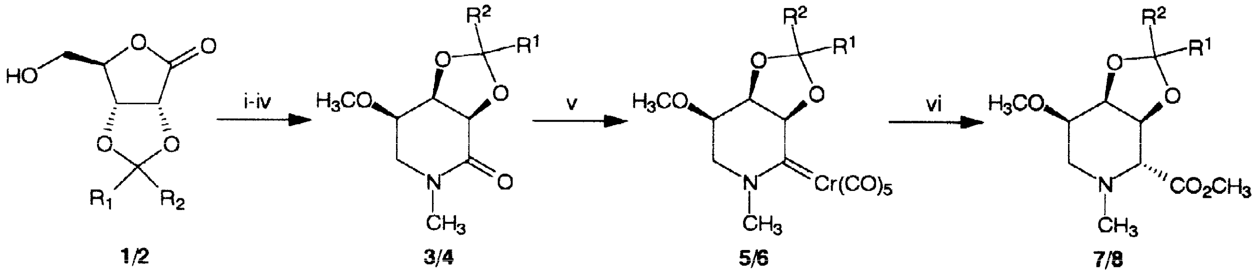
Abstract:

Nucleophilic addition of methanol to ketene equivalents generated by photolysis of pentacarbonyl[1,5-imino-D-ribopyranosylidene]chromium complexes leads diastereospecifically to D-allonates.

Keywords: Carbenes and carbenoids; Carbohydrates; Ketenes; Photochemistry

Fischer-type carbene complexes $(CO)_5Cr=C(XR')R$ (X = O, NR'') have been developed to valuable reagents for stereoselective synthesis.[2] For instance, under UV-conditions aminocarbene complexes serve as ketene equivalents which may be trapped by imine or alcohol nucleophiles to give natural or non-natural β-lactams or α-amino acids.[3] We now describe the preparation of pentacarbonyl[1,5-iminopyranosylidene]chromium complexes **5** and **6** as the first examples of iminopyranoses bearing a metal-stabilized carbene functionality[4] and their application in the synthesis of imino derivatives of aldonates in the D-*allo*-configuration.[5]



Scheme 1: Reagents and conditions
1, **3**, **5**, **7**: $R^1 = R^2 = CH_3$; **2**, **4**, **6**, **8**: $R^1–R^2 = C_5H_{10}$; i) p-TosCl, pyridine, -28°C, 20h; ii) NaN_3, DMF, 100°C, 6h; iii) 6 mol% Pd/C, 1.5 bar H_2, 2h; iv) NaH, DMF, 0°C, 1.5h, then CH_3I, 25°C, 8h; v) $K_2Cr(CO)_5$, THF, -78°C, then TMSCl; vi) CH_3OH, hv, 25°C, 5d.

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Reaction of the sugar lactams **3** and **4**, readily accessible from D-ribono-1,4-lactones **1** and **2**, with $K_2Cr(CO)_5$ in THF followed by TMSCl-assisted deoxygenation leads to iminopyranosylidene complexes **5** and **6** in 72% and 21% yield, respectively.[6] These are modified into methyl aldonates **7** and **8** upon UV-irradiation in methanol at room temperature for 5 days using a 125 W high pressure mercury lamp. Purification by column chromatography affords the D-aldonates in 70% (**7**) and 38% (**8**) isolated yield (Scheme 1). In both cases, the formation of a single diastereomer in the D-*allo*-configuration is indicated within the limits of ^{1}H-NMR spectroscopy;[7] no diastereomeric D-altronate could be detected.

In conclusion, we have shown that the transformation of sugar lactams into chromium-stabilized iminopyranosylidenes and their subsequent photolysis in alcohols provide a novel access to 2,6-imino-aldonic acid derivatives with excellent diastereoselectivity.[8] The scope of this methodology is under current investigation.

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References and Notes:

[1] Organotransition Metal Modified Sugars, part 9; for part 8, see: Dötz, K. H.; Weyershausen, B.; Nieger, M. *Organometallics*, submitted for publication. Review: Dötz, K. H.; Ehlenz, R. *Chem. Eur. J.* **1997**, *3*, 1751.

[2] Reviews: a) Dötz, K. H. *Angew. Chem.* **1984**, *96*, 573; *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 587; b) Wulff, W. D. in *Comprehensive Organometallic Chemistry II*, ed. E. W. Abel, F. G. A. Stone, G. Wilkinson, Pergamon Press, New York, 1995, vol. 12, 470.

[3] Reviews: a) Hegedus, L. S. in *Comprehensive Organometallic Chemistry II*, ed. E. W. Abel, F. G. A. Stone, G. Wilkinson, Pergamon Press, New York, 1995, vol. 12, 549; b) Hegedus, L. S. *Tetrahedron* **1997**, *53*, 4105.

[4] For the preparation of 1,4-iminofuranosylidene complexes see: Dötz, K. H.; Haase, W. C.; Klumpe, M.; Nieger, M. *J. Chem. Soc. Chem. Commun.* **1997**, 1217.

[5] For the synthesis of 2,6-imino-D-aldonic acids in L-*gulo*, L-*ido*-, D-*manno* or L-*galacto*-configuration, see: a) Bashyal, B. P.; Chow, H.-F.; Fleet, G. W. J. *Tetrahedron Lett.* **1986**, *27*, 3205; b) Bashyal, B. P.; Chow, H.-F.; Fellows, F. E.; Fleet, G. W. J. *Tetrahedron* **1987**, *43*, 415; c) Fleet, G. W. J.; Fellows, F. E.; Smith, P. W. *Tetrahedron* **1987**, *43*, 979; d) Fleet, G. W. J.; Ramsden, N. G.; Witty, D. R. *Tetrahedron* **1989**, *45*, 327; e) Tong, M. K.; Blumenthal, E. M.; Ganem, B. *Tetrahedron Lett.* **1990**, *31*, 1683; f) Park, K. H.; Yoon, Y. J.; Lee, S. G. *J. Chem. Soc. Perkin Trans. I* **1994**, 2621.

[6] a) Imwinkelried, R.; Hegedus, L. S. *Organometallics* **1988**, *7*, 702; b) Schwindt, M. A.; Lejon, T.; Hegedus, L. S. *Organometallics* **1990**, *9*, 2814.

[7] The configuration was confirmed by NOE experiments.

[8] Selected spectroscopic data: **3**: α_D^{20} = -3.6° (c 1.006, CH_3OH), m.p.: 65° C. **5**: α_D^{20} = +81.5° (c 0.404, Et_2O); m.p.: 111° C (dec.); ^{13}C-NMR (125 MHz/CD_3OD): δ = 24.4, 26.1 (2 CH_3); 53.5 (NCH_3); 55.6 (C-5); 58.2 (OCH_3); 72.7, 72.9 (C-3, C-4); 86.9 (C-2); 110.1 (Me_2C); 219.3 (4 CO_{cis}); 225.1 (CO_{trans}); 266.5 (C-1). **7**: ^{1}H-NMR (500 MHz/ C_6D_6): δ = 1.26 (s, 3H, CH_3); 1.56 (s, 3H, CH_3); 2.11 (s, 3H, NCH_3); 2.46 (pt, ^2J = 10.72, ^3J = 10.72, 1H, H-6); 2.72 (dd, ^2J = 10.72, ^3J = 5.26, 1H, H-6'); 3.03 (d, ^3J = 8.44, 1H, H-2); 3.15 (s, 3H, OCH_3); 3.38 (s, 3H, CO_2CH_3); 3.49 (ddd, ^3J = 10.72, ^3J = 5.26, ^3J = 3.87, 1H, H-5); 4.23 (dd, ^3J = 4.67, ^3J = 3.87, 1H, H-4); 4.51 (dd, ^3J = 8.44, ^3J = 4.67, 1H, H-3); ^{13}C-NMR (125 MHz/C_6D_6): δ = 26.3, 28.3 (2 CH_3); 43.3 (NCH_3); 51.6 ($CO_2\mathit{C}H_3$); 54.2 (C-6); 55.9 (OCH_3); 70.9 (C-2); 72.2 (C-4); 74.5 (C-5); 76.8 (C-3); 109.9 (Me_2C); 172.5 ($\mathit{C}O_2CH_3$); HR-MS: $C_{12}H_{21}NO_5$ calc.: 259.1419 found: 259.1430. **8**: ^{1}H-NMR (500 MHz/ C_6D_6): δ = 1.20-1.27 (m, 2H); 1.54-1.59 (m, 4H); 1.63-1.72 (m, 2H); 1.83-1.93 (m, 2H); 2.11 (s, 3H, NCH_3); 2.47 (pt, ^2J = 10.83, ^3J = 10.83, 1H, H-6); 2.76 (dd, ^2J = 10.83, ^3J = 5.30, 1H, H-6'); 3.04 (d, ^3J = 8.54, 1H, H-2); 3.17 (s, 3H, OCH_3); 3.39 (s, 3H, CO_2CH_3); 3.58 (m, 1H, H-5); 4.27 (dd, ^3J = 4.57, ^3J = 3.87, 1H, H-4); 4.55 (dd, ^3J = 8.54, ^3J = 4.57, 1H, H-3); HR-MS: $C_{15}H_{25}NO_5$ calc.: 299.1732 found: 299.1741.