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6-*endo* Versus 5-*exo* radical cyclization: streamlined syntheses of carbahexopyranoses and derivatives by 6-*endo-trig* radical cyclization

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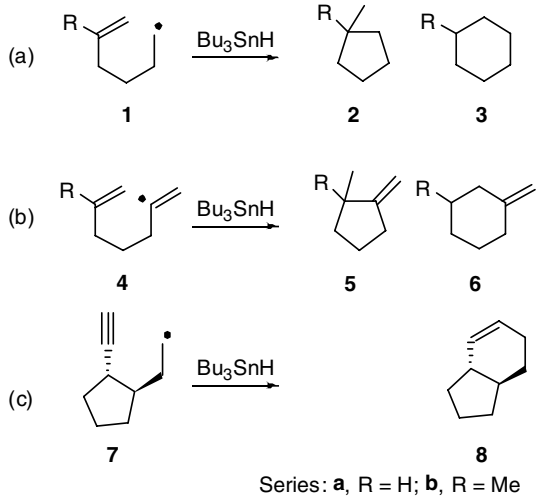
Abstract—Three factors that can direct 6-*endo* radical cyclization over 5-*exo* ring closure: substitution at C-5, vinyl radical cyclization and ring strain, have been considered in the context of the preparation of carbapyranoses from carbohydrate derivatives. As a result, alkyl radicals in substrates containing a strain inducing 2,3-*O*-isopropylidene ring, and vinyl radical in non-strained compounds undergo a completely regioselective 6-*endo-trig* ring closure leading to carbasugar derivatives.

Contrary to predictions based on thermodynamic criteria, the cyclization of 5-hexenyl radicals (e.g., **1a**) generally results in the formation of cyclopentane derivatives (**2a**) via a predominant 5-*exo* mode of closure.[1] This has been rationalized in terms of stereoelectronic[2] control of the reaction and accordingly cyclohexane derivatives (**3a**) arising from 6-*endo* closure are rarely observed. Nevertheless, the regiochemistry of the radical cyclization can be influenced, and even reversed, to favor the formation of six-membered rings by factors other than stereoelectronic control.[3]

Three of the strategies used to favor 6-*endo* selectivity, outlined in Scheme 1, are based on: (1) the substitution pattern at C-5 (Scheme 1a). This result has been ascribed to the presence of an unfavorable steric effect in the 5-*exo* mode of cyclization.[4] Accordingly, cyclization of **1b** yields a 2:3 ratio of *exo*/*endo* products **2b**/**3b** compared to a 49:1 ratio for **2a**/**3a** obtained from the cyclization of **1a**; (2) the vinylic nature of the radical (Scheme 1b). Beckwith[5] and Stork[6] have shown that under tin hydride mediated reaction conditions, the radical cyclization of 1-vinyl-5-hexenyl radicals **4a** gives mixtures of both 5-*exo* and 6-*endo* products (**5a** and **6a**). The kinetic



Scheme 1. 5-*exo*/6-*endo* Radical cyclization of different radicals.

studies of Beckwith also revealed that the formation of methylene cyclohexane **6a** is the result of further isomerization of an initially formed '5-*exo* radical',[5] and therefore low concentrations of stannane favor the isomerization process leading to six-membered rings; (3) the ring strain associated with intermediates such as **7**. Hoffmann and co-workers found that five-membered rings with two appendages, that contain a radical

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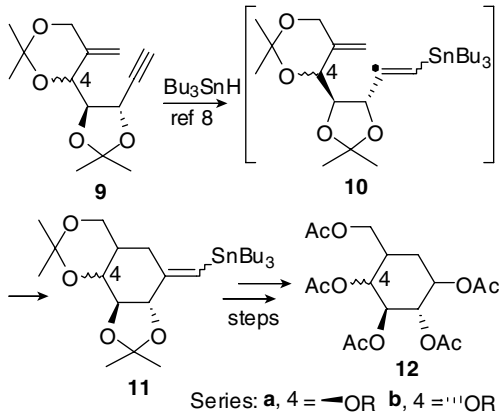


Scheme 2. Synthesis of carbasugars (**12**) by 6-*endo-trig* radical cyclization of enynes (**9**).

and a radical acceptor, in an *anti*-disposition, undergo 6-*endo* closure, **7**→**8**, rather than the potentially faster 5-*exo* cyclization which is prevented by ring strain[7] (Scheme 1c).

In this context, some time ago,[8] we reported a concise entry to carbasugars (e.g., **12**, Scheme 2),[9] based on the entirely regioselective 6-*endo-trig* radical cyclization of enynes **9**, followed by standard transformation of the ensuing alkenyl stannanes (**11**) (Scheme 2). The success of the key transformation (**9**→**11**) was largely based on the above-mentioned *regio*-directing features. More recently, we have shown that 1-vinyl-5-methyl-5-hexenyl radicals **4b** (Scheme 1b), which combine the vinylic nature of the radical and the substitution at C-5 as regiodirecting features, give rise to six-membered ring products (**6b**) as the major isomers prevailing over the isomeric five-membered ring compounds (**5b**).[10]

The nature of our original strategy restricted its use to enynes containing the required strain-inducing 2,3-*anti*-isopropylidene group (e.g., **9a**,**b**). For that reason, we have recently turned our attention to the relative importance of the factors dictating the regiochemical outcome of this radical cyclization, and in this Letter we disclose a general approach to carbapyranoses based on the regioselective 6-*endo-trig* cyclization of more simple sugar precursors.

As candidates for our study, we have prepared *manno*- and *gluco*-derivatives **13**–**18**. *manno*-Derivative **13** was chosen because it was devoid of the 2,3-*anti*-isopropylidene ring, and so were acyclic enynes **14** and **15**. Thionocarbonate[11] **16** and xanthate[12] **17** were selected because while maintaining the 2,3-*anti*-isopropylidene ring would generate intermediate alkyl, rather than vinyl, radicals. Finally, thionocarbonate **18**, that retains only the substitution pattern at C-5 as a regiodirecting factor, was also prepared.

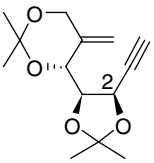
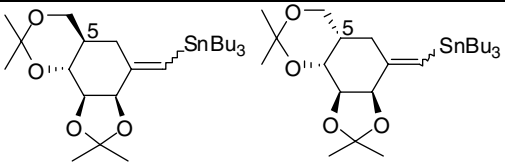
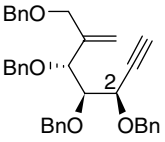
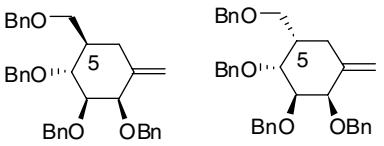
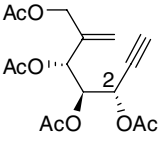
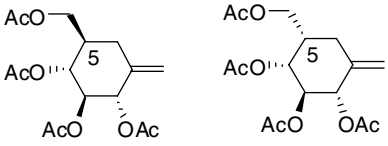
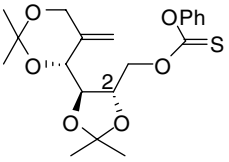
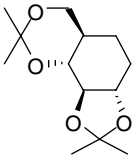
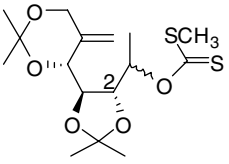
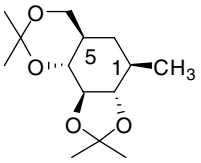
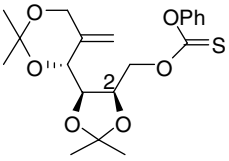
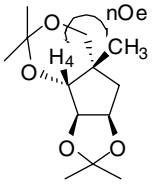
Enyne **13** was synthesized, following our described methodology for the preparation of **9**, starting from 2,3:4,6-di-*O*-isopropylidene-D-*manno* pyranose.[13] Enynes **14** and **15** were prepared from di-*O*-isopropylidene derivatives **13** and **9** by deprotection (THF, AcOH, H_2O) followed by benzylation (NaH, BnBr) or acetylation, respectively. Alkenes **16**–**18** were prepared from 2,3:4,6-di-*O*-isopropylidene-D-*gluco*[14] or D-*manno*[13] pyranoses.

The results obtained are outlined in Table 1. Treatment of enyne **13** with Bu_3SnH and AIBN in toluene (0.02 M, 85 °C, syringe pump addition 6 h, then 12 h more) resulted in the formation of epimeric alkenyl stannanes **19** and **20** as the sole observed regioisomers (Table 1, entry 1). Enyne **14**, under similar reaction conditions, followed by destannylation (THF, AcOH, H_2O), yielded methylenecyclohexanes **21** and **22** (Table 1, entry 2). Likewise, radical cyclization of tetraacetate **15** gave rise to carbasugar precursors **23** and **24** (Table 1, entry 3). Radical cyclizations of *gluco*-thionocarbonate **16** and xanthate **17** took place with complete *endo*-selectivity to yield carbasugar derivatives **25** and **26** (Table 1, entries 4 and 5). On the contrary, radical cyclization of *manno*-thionocarbonate **18** took place with complete *exo*-selectivity to generate cyclopentane **27** (Table 1, entry 6).

The stereochemistry at C-5 in compounds **19**–**26** was unambiguously established based on the observed vicinal coupling constants (e.g., $J_{4,5}$). For instance, the assignment of the stereochemistries at C-1 and C-5 in compound **26** was made as follows: the axial nature for H-2 and the β-configuration for the methyl group at C-1 were inferred from the observed coupling constants, $J_{1,2}$ and $J_{2,3}$ (8.7 and 9.0 Hz, respectively). Other observed coupling constants: $J_{3,4} = 9.0$ and $J_{4,5} = 9.0$ Hz, allowed us to propose a $^4C_1$ conformation for **26**, and a β-configuration for the hydroxymethyl group at C-5 (D-series). The stereochemistry at the quaternary center in compound **27** was rigorously assigned on the basis of an observed NOE between H-4 and the methyl group.

From the results in Table 1, some conclusions can be inferred. Substrates that incorporate two regiodirecting features: (a) vinyl radical and substitution at C-5 (compounds **13**–**15**, Table 1 entries 1–3) or (b) ring strain and substitution at C-5 (compounds **16** and **17**, Table 1, entries 4 and 5) undergo 6-*endo-trig* radical cyclization. However, thionoformate **18**, where the substituent at C-5 was the only regiodirecting factor, underwent 5-*exo-trig* ring closure exclusively. On the other hand, the bicyclic nature of enyne **13** or the linear nature of **14** do not seem to influence the regiochemistry of the process, although they do have a profound influence on its stereoselectivity (Table 1, compare entries 1 and 2). The radical cyclization of enyne **14** is noteworthy since no competing intramolecular hydrogen transfer (e.g., 1,5-H) from the benzyl groups was observed. A primary, rather than a vinyl, radical ensuing from Barton–McCombie type deoxygenation of thionocarbonate **16** also underwent an efficient cyclization to yield 1-deoxy-5a-carba-D-glucopyranose derivative **25**, which for the purpose of characterization was transformed into its corresponding tetra-*O*-acyl derivative. Deoxygenation of secondary xanthate **17**, was also followed

Table 1. Radical cyclization of carbohydrate derivatives **13**–**18** mediated by Bu_3SnH and AIBN

Entry	Starting material	Products	Yield (%)
1	 **13**	 **19** (15:1) **20**	64[a]
2	 **14**	 **21** (1.6:1) **22**	80[a,b]
3	 **15**	 **23** (1.4:1) **24**	64[a,b]
4	 **16**	 **25**	62[a]
5	 **17**	 **26**	64[a]
6	 **18**	 **27**	76[a]

Reaction conditions: (a) Bu_3SnH, AIBN, 0.02 M (initial concentration of the substrate), toluene, 85 °C, syringe pump addition; (b) THF, AcOH, H_2O (4:2:1), room temperature.

by radical cyclization to yield, in stereoselective manner, carbapyranose C-glycoside derivative **26**. However, different radical precursors related to **17** where the methyl groups at C-1 have been replaced by *n*-butyl, allyl or alkynyl groups did not lead, upon similar treatment with Bu_3SnH and AIBN, to synthetically useful amounts of the expected carbasugar C-glycosides.[15]

In summary, we have found that simple unsaturated carbohydrate systems are able to undergo 6-*endo-trig* radical cyclization leading to carbapyranose derivatives. These systems have been rationally devised and they must include at least one regiodirecting feature (vinyl radical or ring strain) in addition to the 'substitution at C-5'. The method allows the synthesis of carbapyranose *exo*-glycals[16,17] (e.g., **21**–**24**) and has also been proven useful in the preparation of a methyl C-glycoside of a carbasugar, **26**.[18–20]

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15. These cyclization reactions led to complex reaction mixtures that included the corresponding deoxygenated compounds and minor amounts of stereoisomeric cyclized products. For instance, from the reaction of the allyl analogue of methyl xanthate **17** we could isolate a compound resulting from deoxygenation (23%) as well as two isomeric *C*-allyl carbasugars (6% and 10% yield).
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18. *General procedure for the radical cyclization*: A thoroughly degassed solution of the substrate (1 mmol) in toluene (0.02 M) was heated at 80 °C under argon. A solution of Bu_3SnH (1.5 equiv) and AIBN (0.3 equiv) was then added in toluene (3 mL) via a syringe driven pump over 6 h. Heating was then continued for 12 h. After cooling, the reaction mixture was concentrated in vacuo and the residue was purified by flash chromatography (hexane–EtOAc 97.5:2.5).
19. *General procedure for destannylation*: The crude reaction mixture from the above radical cyclization was dissolved in a mixture of AcOH–THF–H_2O (2:4:1) (50 mL) and heated to reflux overnight. The solvent was then evaporated and the methylene cyclohexanes were purified by flash chromatography (hexane–ethyl acetate).
20. *Data for selected compounds*: Enyne **13**: $[\alpha]_D$ −40.0 (*c* 0.92, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) 1.35 (s, 3H), 1.42 (s, 3H), 1.46 (s, 3H), 1.56 (s, 3H), 2.54 (d, $J = 2.2$ Hz, 1H), 4.27 (dd, $J = 1.4$, 14.2 Hz, 2H), 4.37 (t, $J = 6.0$ Hz, 1H), 4.70 (m, 1H), 4.84 (dd, $J = 6.0$, 2.1 Hz, 1H), 4.97 (br s, 2H); ^{13}C NMR (50 MHz, $CDCl_3$): δ (ppm) 23.0, 26.0, 27.0, 27.3, 53.4, 64.2, 67.4, 71.6, 78.0, 79.4, 100.1, 108.6, 110.8, 142.8, 177.0. Enyne **14**: $[\alpha]_D$ −59.6 (*c* 0.3, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) 2.40 (d, $J = 3.0$ Hz, 1H), 3.77 (t, $J = 5.3$ Hz, 1H), 3.85 (d, $J = 12.0$ Hz, 1H), 3.94 (d, $J = 12.0$ Hz, 1H), 4.19 (dd, $J = 11.6$, 4.4 Hz, 1H), 4.29 (dd, $J = 5.6$, 2.0 Hz, 1H), 4.36–4.85 (m, 8H), 5.30 (br s, 2H), 7.19–7.36 (m, 20H); ^{13}C NMR (50 MHz, $CDCl_3$): δ (ppm) 69.8, 75.3, 81.0, 81.8, 70.3, 70.6, 71.2, 72.7, 75.1, 116.8, 127.4 (×2), 127.5 (×4), 127.8 (×2), 127.9 (×2), 128.0 (×2), 128.2 (×4), 128.3 (×4), 137.8, 138.2, 138.3, 138.5, 142.5; API-ES positive: 555.5 $(M+Na)^+$. Enyne **15**: $[\alpha]_D$ +46.9 (*c* 1.02, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) 2.09 (s, 3H), 2.12 (s, 3H), 2.13 (s, 6H), 2.56 (d, $J = 2.0$ Hz, 1H), 4.57 (d, $J = 13.2$ Hz, 1H), 4.71 (d, $J = 13.2$ Hz, 1H), 5.31 (d, $J = 14.0$ Hz, 1H), 5.48 (dd, $J = 3.6$, 7.0 Hz, 1H), 5.57 (dd, $J = 2.0$, 7.0 Hz, 1H), 5.67 (d, $J = 3.6$ Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): δ (ppm) 20.6, 20.8, 20.9, 21.0, 29.0, 62.9, 64.4, 72.0, 72.1, 76.3, 80.9, 81.6, 111.7, 118.3, 139.1, 169.5 (×2), 170.6 (×2); API-ES positive: 363.3 $(M+Na)^+$, 358 $(M+NH_4)^+$. *Methylene cyclohexanes* **19**: (4:1 mixture of unassigned *Z*, *E* stannanes); ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) 0.87 (t, $J = 7.2$, 9H), 0.89 (m, 6H), 1.24 (m, 6H), 1.27 (s, 3H), 1.29 (s, 3H), 1.30 (m, 6H), 1.31 (s, 3H), 1.33 (s, 3H), 1.91 (dd, $J = 2.9$, 10.4 Hz, 1H), 2.12 (m, 2H), 3.62

(t, $J = 8.5$ Hz, 1H), 3.75 (m, 2H), 4.12 (dd, $J = 4.3$, 5.9 Hz, 1H), 4.58 (d, $J = 4.3$ Hz, 1H), 6.12 (s, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): δ (ppm) 10.0 (×3), 13.5 (×3), 26.1, 27.0, 27.1 (×3), 28.2, 28.9 (×3), 29.5, 32.3, 35.7, 64.0, 74.7, 79.2, 81.3, 98.9, 109.3, 133.4, 148.2; MS: 544 $(M+1)^+$. *Methylene cyclohexanes* **20**: (one isomer) ^{1}H NMR (200 MHz, $CDCl_3$): δ (ppm) 0.87 (m, 9H), 0.89 (m, 6H), 1.24 (m, 6H), 1.27 (s, 3H), 1.28 (s, 3H), 1.29 (m, 6H), 1.33 (s, 3H), 1.35 (s, 3H), 2.02 (m, 1H), 2.61 (m, 2H), 3.54 (dd, $J = 2.2$, 11.5 Hz, 1H), 4.00 (m, 3H), 4.43 (d, $J = 7.1$ Hz, 1H), 5.91 (s, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): δ (ppm) (one isomer) 10.2 (×3), 13.5 (×3), 26.5, 27.0 (×3), 28.9 (×4), 29.4, 29.6, 34.9, 36.4, 68.2, 75.1, 79.5, 79.5, 81.3, 99.0, 109.3, 133.4, 148.0; MS: 544 $(M+1)^+$. *Carbasugar derived exo-glycals* **23** *and* **24** *(mixture)*: ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 1.68 (m, 2H), 2.02 (m, 1H), 2.03 (s, 3H), 2.04 (s, 3H), 2.04 (s, 3H), 2.06 (s, 3H), 2.08 (s, 3H), 2.09 (s, 3H), 2.11 (s, 3H), 2.13 (s, 3H), 2.16 (m, 2H), 2.52 (m, 2H), 4.02 (m, 3H), 4.09 (dd, $J = 5.0$, 11.6 Hz, 1H), 4.24 (dd, $J = 5.0$, 10.6 Hz, 1H), 5.10 (m, 7H), 5.91 (m, 2H); ^{13}C NMR (50 MHz, $CDCl_3$): δ (ppm) 20.4 (×2), 20.5, 20.6 (×2), 20.7, 20.8 (×2), 26.7, 27.8, 31.0, 33.0, 36.3, 40.1, 61.6, 63.2, 71.2, 71.4, 71.5, 72.9, 73.1, 74.9, 110.1, 113.2, 137.7, 139.2, 169.8, 169.9, 170.0, 170.1, 170.5 (×2), 170.6, 170.8; API-ES: 365 $(M+Na)^+$. *Carbasugar* **25**: $[\alpha]_D$ −5.6 (*c* 0.7, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): δ (ppm) 1.43 (s, 6H), 1.44 (s, 6H), 2.1 (m, 4H), 3.65 (m, 6H); ^{13}C NMR (50 MHz, $CDCl_3$): δ (ppm) 19.3, 22.3, 26.8, 27.4, 29.7, 30.6, 39.4, 64.4, 73.8, 75.4, 78.3, 99.0, 110.6. It was characterized as its corresponding tetra-*O*-acetyl derivative: $[\alpha]_D$ +18.6 (*c* 0.14, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 1.87 (m, 1H), 1.96 (m, 1H) 2.00 (s, 6H), 2.01 (s, 3H), 2.02 (s, 3H), 2.15 (m, 1H), 3.94 (dd, $J = 3.4$, $J = 9.0$ Hz, 1H), 4.05 (dd, $J = 5.0$, 9.0 Hz, 1H), 4.88 (m, 1H), 4.96 (t, $J = 9.6$, 1H), 5.07 (t, $J = 9.6$, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): δ (ppm) 15.2, 20.7, 23.5, 28.4, 29.7, 40.2, 43.9, 63.6, 71.8, 72.2, 75.0, 170.1, 170.2 (×2), 171.0; API-ES positive: 353 $(M+Na)^+$. *Carbasugar* **26**: $[\alpha]_D$ −8.4 (*c* 0.2, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 1.41 (s, 12H), 1.48 (s, 3H), 1.53 (m, 1H), 1.60 (m, 1H), 1.74 (m, 1H), 1.88 (m, 1H), 3.04 (dd, $J = 9.0$, 8.8 Hz, 1H), 3.44 (t, $J = 9.0$ Hz, 1H), 3.71 (m, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ (ppm) 17.5, 26.8 (×2), 27.8 (×2), 32.5, 34.2, 39.0, 64.4, 73.9, 80.3, 83.7, 99.9, 110.9; API-ES positive: 535 $(2M+Na)^+$, 279 $(M+Na)^+$. *Cyclopentane* **27**: ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 1.07 (s, 3H), 1.27 (s, 3H), 1.32 (s, 3H), 1.38 (s, 3H), 1.48 (s, 3H), 1.59 (d, $J = 14.4$ Hz, 1H), 2.38 (dd, $J = 14.4$, 6.3 Hz, 1H), 3.40 (t, $J = 12.0$ Hz, 1H), 3.60 (d, $J = 12.0$ Hz, 1H), 3.94 (s, 1H), 4.37 (d, $J = 6.0$ Hz, 1H), 4.77 (t, $J = 6.3$ Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): δ (ppm) 18.6, 21.7, 23.1, 25.5, 29.1, 38.9, 39.4, 66.7, 80.1, 80.7, 87.0, 97.4, 109.8; API-MS positive: 265 $(M+Na)^+$.