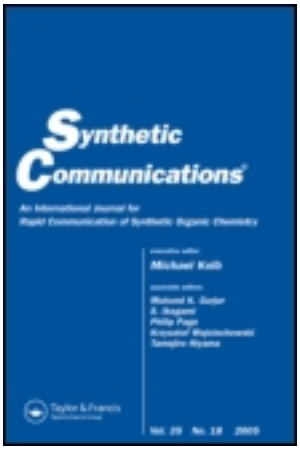

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An Improved Procedure for the Conversion of Alkenes and Glycals to 1,2-Diazides Using $Mn(OAc)_3 \cdot 2H_2O$ in Acetonitrile Containing Trifluoroacetic Acid

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AN IMPROVED PROCEDURE FOR THE CONVERSION OF ALKENES AND GLYCALS TO 1,2-DIAZIDES USING $Mn(OAc)_3 \cdot 2H_2O$ IN ACETONITRILE CONTAINING TRIFLUOROACETIC ACID

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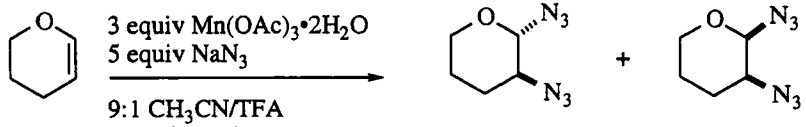
Abstract: Alkenes and Glycals react with $Mn(OAc_3) \cdot 2H_2O$ and NaN_3 in 9:1 acetonitrile-trifluoroacetic acid to give 1,2-diazides in >80% yield. Allylic azides are formed by slow addition of NaN_3 to a mixture of alkene, $Mn(OAc)_3 \cdot 2H_2O$ and $Cu(OAc)_2$.

In 1985, Fristad and coworkers reported that simple alkenes are converted to 50-75% of the corresponding 1,2-diazide by reaction with $Mn(OAc)_3 \cdot 2H_2O$ and excess NaN_3 in AcOH at 70-116 °C for 10-30 min.[1-3] Extension of this procedure to glycals to provide 2-azido-2-deoxyglycopyranosyl azides would be of synthetic utility since glycopyranosyl azides have been extensively used for the preparation of glycosylated asparagine derivatives,[4,5] while 2-azido-2-deoxyglycopyranosyl donors have been extensively used as intermediates for the preparation of 2-amino-2-deoxyglycose containing oligosacharrides.[6-8] These donors were first prepared as a mixture of stereoisomers by Lemieux and Ratcliffe by conversion of the glycal to the 2-azido-2-deoxyglycopyranosyl nitrate with ceric ammonium nitrate and sodium azide in acetonitrile as the first step.[6] 2-Azido-2-deoxyglycopyranosyl phenyl selenides have been prepared as mixtures of stereoisomers by addition of sodium azide and diphenyldiselenide in the presence of (diacetoxyiodo)benzene[9] to peracetylated glycals.[8]

Initial experiments were conducted with dihydropyran (**1**) as a glycal model. Protonation of the enol ether double bond of **1** is faster than azide oxidiation under Fristad's conditions with $Mn(OAc)_3 \cdot 2H_2O$ and excess NaN_3 in AcOH at reflux so

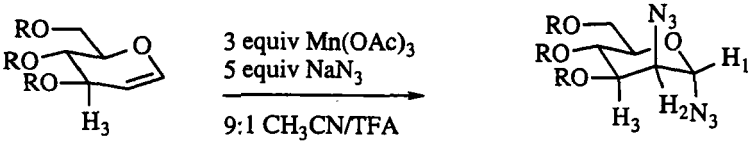
that tetrahydropyranol and tetrahydropyranyl azide are the major products. We eventually found that azide oxidation can be accomplished with very little enol ether protonation by carrying out the reaction in 9:1 acetonitrile-trifluoroacetic acid (MeCN-TFA)[10] at low temperature. Reaction of **1** as a 0. 1 M solution with 3 equiv of $Mn(OAc)_3 \cdot 2H_2O$ and 5 equiv of NaN_3 in 9:1 MeCN-TFA for 3 min at -20 °C provides 86% of a 94:6 inseparable mixture of trans and cis diazides **2** and **3** and <10% of tetrahydropyranol and tetrahydropyranyl azide resulting from protonation of the double bond. The stereochemistry is assigned based on the coupling between the methine hydrogens which should be larger for the diaxial hydrogens in the trans isomer **2** (6.6 Hz) than for the equatorial and axial hydrogens in the cis isomer **3** (3.7 Hz).



1 **2** (81%) **3** (5%)

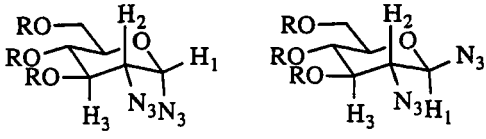
This solvent mixture works equally well with peracetylated or perbenzylated glycals. Reaction of 3,4,6-tri-*O*-acetyl-D-glucal (**4a**) with 3 equiv of $Mn(OAc)_3 \cdot 2H_2O$ and 5 equiv of NaN_3 in 9:1 MeCN-TFA for 2 h at 25 °C provides 92% of a partially separable 52:31:17 mixture of **5a**, **6a** and **7a**. A similar reaction with 3,4,6-tri-*O*-acetyl-D-galactal (**8**) yields 83% of a 60:40 mixture of **9**[11] and **10**.[11] The stereochemistry of the products was assigned based on the coupling pattern of H_2 which absorbs as a doublet of doublets: **5a** (J = 3.3, 1.6 Hz), **6a** (J = 10.3, 4.1 Hz), **7a** (J = 9.9, 9.0 Hz), **9** (J = 10.9, 4.3 Hz), and **10** (J = 10.7, 8.9 Hz). H_1, H_2 and H_3 are all axial in **7a** and **10**, in which H_2 has two large coupling constants, H_2 and H_3 are axial and H_1 is equatorial in **6a** and **10**, in which H_2 has one large coupling constant, and H_3 is axial and H_1 and H_2 are equatorial in **5a**, which has two small coupling constants.

Azide addition to 3,4,6-tri-*O*-benzyl-D-glucal (**4b**) for 2 h at 0 °C affords 81% of an inseparable 41:32:27 mixture of **5b**, **6b** and **7b**. The stereochemistry was assigned by analogy to **5a-7a** based on the coupling constant between H_1 and H_2. Oxidation of the benzyl groups to benzaldehyde occurs at 25 °C. As expected the mixtures of stereoisomers produced from **4a**, **4b**, and **8** are similar to those formed in glycal azidonitrations,[6,7] and azidophenylselenations[8] since all of these processes involve the addition of the azide radical to the glycal double bond.



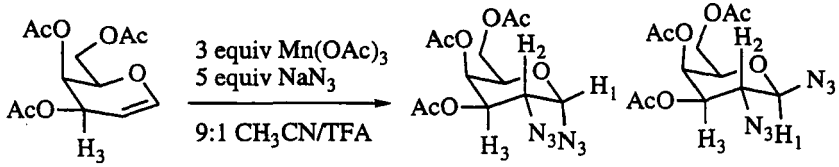
4a, R = Ac
4b, R = Bn

5a, R = Ac (48%)
5b, R = Bn (33%)



6a, R = Ac (28%)
6b, R = Bn (26%)

7a, R = Ac (16%)
7b, R = Bn (22%)

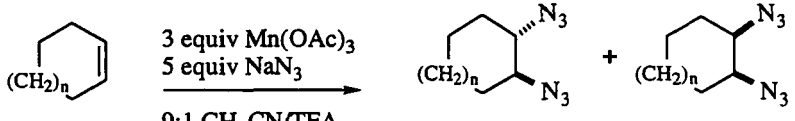


8

9 (50%)

10 (33%)

Azide addition to simple alkenes proceeds in higher yields and is much faster in 9:1 MeCN-TFA than in acetic acid. Cyclohexene (**11a**) affords 88% of a 3:1 mixture of **12a**[12] and **13a**[12] in 5 min at -20 °C versus 59% of a 4:1 mixture in acetic acid at 85 °C.[1] Similarly cyclooctene (**11b**) affords 74% of a 5:1 mixture of **12b** and **13b** in 5 min at -20 °C versus 51% of 6:1 mixture in acetic acid at 85 °C.[1] Since addition of azide to cyclohexene and dihydropyran occurs at similar rates, the reaction proceeds by oxidiation of azide rather than oxidation of the alkene to a cation-radical, which would occur much more rapidly for dihydropyran than for cyclohexene.



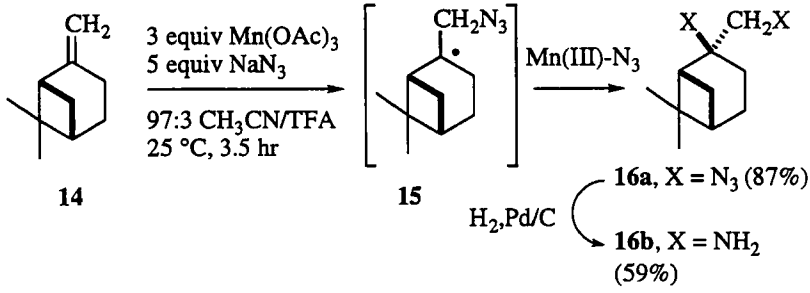
11a, n = 1
11b, n = 3

12a, n = 1 (66%)
12b, n = 3 (62%)

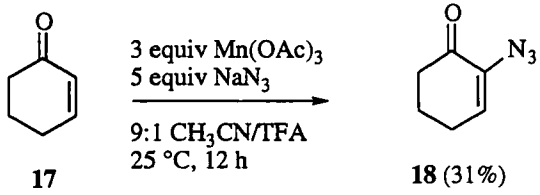
13a, n = 1 (22%)
13b, n = 3 (12%)

Even though TFA is a much stronger acid than acetic acid, double bond protonation is less of a problem in MeCN-TFA mixtures than in acetic acid, presumably because the TFA accelerates oxidation of azide anion more than it accelerates protonation of the double bond. The very acid-sensitive β-pinene (**14**)

decomposes in 9:1 MeCN-TFA, but gives diazide **16a** stereospecifically in 87% yield in 97:3 MeCN-TFA (3.5 h, 25 °C) without accompanying opening of the strained four-membered ring. This suggests that conversion of intermediate radical **15** to diazide **16a**, probably by ligand transfer from a Mn(III) azide,[1] is exceedingly rapid, since opening of the cyclobutylcarbinyl radical of **15** should proceed with a rate constant of about 10^5 s^{-1}.[13,14] Hydrogenation of **16a** over 5% Pd/C in EtOH at 1 atm H_2 provides 59% of diamine **16b**, which may be a useful ligand for asymmetric synthesis.

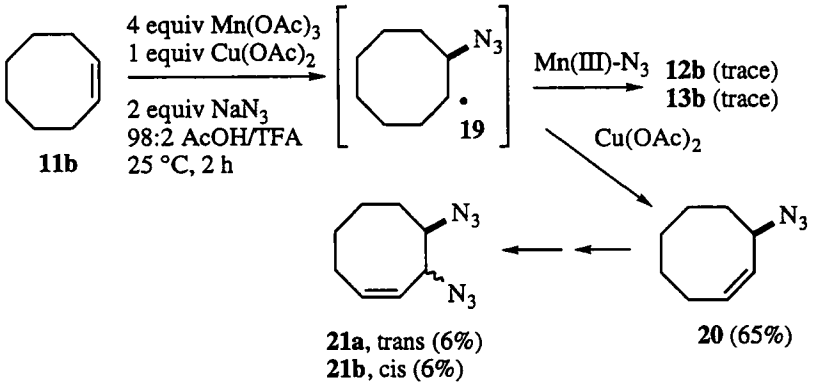


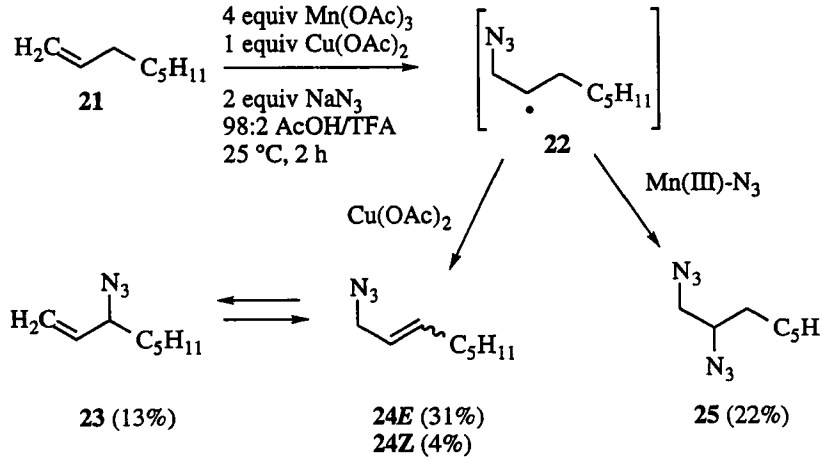
The electrophilic azide radical will even add to α,β-unsaturated enones in 9:1 MeCN-TFA. Addition of azide to 2-cyclohexenone (**17**) over 12 h at 25 °C affords 31% of 2-azido-2-cyclohexenone (**18**).[15] 2,3-Diazidocyclohexanone can be detected spectroscopically, but eliminates hydrazoic acid under the reaction conditions to give **18**.



Primary and secondary radicals formed in Mn(III)-based oxidative free-radical cyclizations can be oxidized to alkenes by $Cu(OAc)_2$.[16] We investigated the oxidation of alkenes with $Mn(OAc)_3 \cdot 2H_2O$, $Cu(OAc)_2$, and NaN_3 to determine whether oxidation of the intermediate β-azidoalkyl radical by $Cu(OAc)_2$ to give an allylic azide could compete with ligand transfer from a Mn(III) azide to give a 1,2-diazide. Reaction of $Mn(OAc)_3 \cdot 2H_2O$, $Cu(OAc)_2$, and NaN_3 with cyclooctene in 9:1 MeCN-TFA gives a 1:20 mixture of allylic azide **20** and diazides **12b** and **13b**, indicating that azide transfer is much faster than oxidation by Cu(II) in this solvent mixture. Better results are obtained in 98:2 AcOH-TFA, which affords a 3:1

mixture of allylic azide **20** and diazides **12b** and **13b**. The best results are obtained by slow addition (1.5 h) of a solution of sodium azide in AcOH with a syringe pump to a solution of 4 equiv of $Mn(OAc)_3 \cdot 2H_2O$, 1 equiv of $Cu(OAc)_2$ and cyclooctene in 98:2 AcOH-TFA at 25 °C. These conditions provide 65% of allylic azide **20**, only traces of diazides **12b** and **13b**, and 12% of allylic diazides **21a** and **21b**, which are formed by azide addition to allylic azide **20**. Under these conditions cyclohexene undergoes mainly allylic oxidation to give 2-cyclohexenyl acetate as has been previously observed with $Co(OAc)_3$.[17] A similar reaction with





1-octene (**21**) affords 22% of diazide **25** and 48% of a 28:65:7 mixture of allylic azides **23**, **24*E*** and **25*Z***,[18] which are known to equilibrate readily at room temperature.[18] Thus it is possible to trap β-azidoalkyl radicals **19** and **22** with $Cu(OAc)_2$, rather than with Mn(III)-N_3, if the azide concentration is kept low. This

provides an efficient route to allylic azides that may be of synthetic value for symmetrical azides such as **20**.

In conclusion, we have shown that 2-azido-2-deoxyglycopyranosyl azides **5-7**, and **9-10**, can be prepared from glycals and $Mn(OAc)_3 \cdot 2H_2O$ and NaN_3 in 9:1 MeCN-TFA and that this solvent mixture permits the use of electron deficient alkenes such as 2-cyclohexenone (**17**). Acid-sensitive alkenes such as β-pinene (**14**) can be used successfully in 97:3 MeCN-TFA. Finally allylic azides can be prepared by slow addition of NaN_3 in AcOH to $Mn(OAc)_3 \cdot 2H_2O$, $Cu(OAc)_2O$, and an alkene in 98:2 AcOH-TFA at 25 °C. These protocols significantly extend the scope of azide addition to alkenes using $Mn(OAc)_3$.

Experimental Section

General Procedures. NMR spectra were recorded at 300 MHz in $CDCl_3$, chemical shifts are reported in δ and coupling constants in Hz and IR spectra are reported in cm^{-1}.

***trans*- and *cis*-1,2-Diazidotetrahydropyran (2, 3).** Dihydropyran (**1**) (0.061 mL, 0.5 mmol) and TFA (0.45 mL) were added to a suspension of $Mn(OAc)_3 \cdot 2H_2O$ (402 mg, 1.5 mmol) and NaN_3 (162.5 mg, 2.5 mmol) in 4.5 mL of MeCN at -20 °C under N_2. The reaction was complete in 3 min. Saturated $NaHSO_3$ aqueous solution was added. The mixture was extracted with CH_2Cl_2 (3 × 15 mL). The combined organic layers were washed with saturated Na_2CO_3 aqueous solution, brine, dried (Na_2SO_4) and concentrated *in vacuo*. Flash chromatography of the residue on silica gel (10:1 hexane-EtOAc) gave 72.4 mg (86%) of an inseparable 94:6 mixture of **2** and **3**: ^1H NMR (**2**) 4.64 (d, 1, J = 6.6), 3.99 (m, 1), 3.57 (m, 1), 3.27 (m, 1), 1.38-2.20 (m, 4); (**3**) 5.20 (d, 1, J = 3.7), 4.40 (m, 1), 3.82 (m, 1), 3.67 (m, 1), 1.38-2.20 (m, 4); ^{13}C NMR (**2**) 89.9, 65.0, 59.2, 26.2, 22.5; (**3**) 88.4, 61.5, 57.5, 23.1, 23.0; IR (neat) 2954, 2864, 2105, 1253.

Azide Addition to 4a. TFA (0.45 mL) was added to a suspension of $Mn(OAc)_3 \cdot 2H_2O$ (402 mg, 1.5 mmol), NaN_3 (162.5 mg, 2.5 mmol), and **4a** (136 mg, 0.5 mmol) in 4.5 mL of MeCN at -20 °C under N_2. The reaction was warmed up to 25 °C and stirred for 2 h. Work up as described above followed by flash chromatography of the residue on silica gel (2:2:1 hexane-CH_2Cl_2-EtOAc) gave 11 mg of **5a**, followed by 91 mg of a 63:37 mixture of **5a** and **6a**, 20 mg of a 55:45 mixture of **5a** and **6a**, 40 mg of a 16:21:63 mixture of **5a**, **6a** and **7a**, and 3 mg of crystalline **7a**. The total yield is 165 mg (92%) of a 52:31:17 mixture of **5a**, **6a** and **7a**: IR (neat, mixture) 2959, 2111, 1749.

Data for 3,4,6-tri-*O*-acetyl-2-azido-2-deoxy-α-D-mannopyranosyl azide (**5a**): ^1H NMR 5.41 (d, 1, J = 1.6), 5.30 (dd, 1, J = 9.8, 9.5), 5.29 (dd, 1, J = 9.5, 3.3), 4.28 (dd, 1, J = 12.4, 5.0), 4.16 (dd, 1, J = 12.4, 2.3), 4.10 (m, 1), 3.96 (dd, 1, J = 3.3, 1.6), 2.12 (s, 3), 2.10 (s, 3), 2.06 (s, 3); ^{13}C NMR 170.6, 169.8, 169.4, 87.8, 70.6, 70.3, 65.3, 61.8, 61.0, 20.7, 20.6, 20.5.

Data for 3,4,6-tri-*O*-acetyl-2-azido-2-deoxy-α-D-glucopyranosyl azide (**6a**) were determined from the 45:55 mixture with **5a**: ^1H NMR 5.47 (d, 1, J = 4.1),

5.36 (dd, 1, J = 10.3, 9.3), 5.03 (t, 1, J = 9.3), 4.29 (dd, 1, J = 12.0, 4.4), 4.18 (m, 1), 4.12 (dd, 1, J = 12.0, 2.3), 3.66 (dd, 1, J = 10.3, 4.1), 2.10 (s, 3), 2.09 (s, 3), 2.04 (s, 3); ^{13}C NMR 170.4, 169.7, 169.6, 87.8, 70.7, 69.7, 68.0, 61.5, 60.7, 20.6, 20.5, 20.5.

Data for 3,4,6-tri-*O*-acetyl-2-azido-2-deoxy-β-D-glucopyranosyl azide (**7a**): ^{1}H NMR 5.04 (m, 2), 4.64 (d, 1, J = 9.0), 4.30 (dd, 1, J = 12.5, 4.7), 4.14 (dd, 1, J = 12.5, 2.3), 3.77 (m, 1), 3.41 (dd, 1, J = 9.9, 9.0), 2.10 (s, 6), 2.03 (s, 3); ^{13}C NMR 170.6, 169.8, 169.5, 89.1, 73.9, 72.9, 67.8, 63.6, 61.6, 20.7, 20.6, 20.5; IR (neat) 2961, 2112, 1747.

Azide Addition to 4b. TFA (0.22 mL) was added to a suspension of $Mn(OAc)_3$•$2H_2O$ (226 mg, 0.87 mmol), NaN_3 (135 mg, 2.0 mmol) and **4b** (98 mg, 0.235 mmol) in 2.2 mL of MeCN at -20 °C under N_2. The reaction was warmed up to 0 °C and stirred for 2 h. Work up as described above followed by flash chromatography of the residue on silica gel (2:2:1 hexane-CH_2Cl_2-EtOAc) gave 15 mg of a 54:39:8 mixture of **5b**, **6b**, and **7b**, followed by 64.8 mg of a 41:34:25 mixture of **5b**, **6b**, and **7b**, and 13 mg of a 27:13:60 mixture of **5b**, **6b** and **7b**. The total yield is 92.8 mg (81%) of a 41:32:27 mixture of **5b**, **6b** and **7b**: IR (neat, mixture) 3031, 2917, 2108.

Partial data for 3,4,6-tri-O-benzyl-2-azido-2-deoxy-α-D-mannopyranosyl azide (**5b**): ^{1}H NMR 5.34 (d, 1, J = 2.0); ^{13}C NMR 88.2, 78.9, 75.2, 73.8, 73.8, 73.6, 73.0, 68.3, 61.0.

Partial data for 3,4,6-tri-O-benzyl-2-azido-2-deoxy-α-D-glucopyranosyl azide (**6b**): ^{1}H NMR 5.42 (d, 1, J = 4.1), 3.58 (dd, 1, J = 4.1, 9.8); ^{13}C NMR 88.3, 80.4, 77.7, 75.7, 75.0, 73.6, 73.0, 67.9, 63.1;

Partial data for 3,4,6-tri-O-benzyl-2-azido-2-deoxy-β-D-galactopyranosyl azide (**7b**): ^{1}H NMR 3.31 (t, 1, J = 9.3); ^{13}C NMR 89.1, 83.3, 77.3, 77.2, 75.7, 75.1, 73.6, 68.1, 66.0.

Azide Addition to 8. TFA (0.45 mL) was added to a suspension of $Mn(OAc)_3$•$2H_2O$ (380 mg, 1.34 mmol), NaN_3 (239 mg, 2.23 mmol) and 3,4,6-tri-O-acetyl-D-galactal (121.5 mg, 0.446 mmol) in 4.5 mL of MeCN at -20 °C under N_2. The reaction was warmed up to 25 °C and stirred for 2 h. Work up as described above followed by flash chromatography of the residue on silica gel (2:2:1 hexane-CH_2Cl_2-EtOAc) gave 17 mg of **9**, followed by 87 mg of a 60:40 mixture of **9** and **10** and 14 mg of a 1:9 mixture of **9** and **10**. The total yield is 118 mg (82.5%) of a 60:40 mixture of **9** and **10**: IR (neat, mixture) 2967, 2115, 1748.

Data for 3,4,6-tri-*O*-acetyl-2-azido-2-deoxy-α-D-galactopyranosyl azide (**9**): ^{1}H NMR 5.50 (d, 1, J = 4.3), 5.44 (dd, 1, J = 1.4, 3.1), 5.20 (dd, 1, J = 3.1, 10.9), 4.36 (m, 1), 4.12 (m, 2), 3.92 (dd, 1, J = 10.9, 4.3), 2.16 (s, 3), 2.06 (s, 3), 2.06 (s, 3); ^{13}C NMR 170.4, 169.8, 169.5, 88.0, 68.6, 68.5, 66.9, 61.2, 57.0, 20.4, 20.3, 20.1. The ^{1}H NMR data are identical to those previously reported.[11]

Data for 3,4,6-tri-O-acetyl-2-azido-2-deoxy-β-D-galactopyranosyl azide (**10**) were determined from the 9:1 mixture with **9**: ^{1}H NMR 5.37 (dd, 1, J = 1.0, 2.8), 4.85 (dd, 1, J = 10.7, 2.8), 4.61 (d, 1, J = 8.9), 4.15 (m, 2), 3.96 (t, 1, J = 10.7), 3.59 (dd, 1, J = 10.7, 8.9), 2.17 (s, 3), 2.06 (s, 3), 2.06 (s, 3); ^{13}C NMR 170.3, 169.9, 169.6, 89.0, 72.5, 71.2, 66.9, 61.0, 60.3, 20.6, 20.6, 20.5. The ^{1}H NMR data are identical to those previously reported.[11]

***trans*- and *cis*-1,2-Diazidocyclohexane (12a, 13a).** Cyclohexene (0.051 mL, 0.5 mmol) and 0.45 mL TFA were added to a suspension of

$Mn(OAc)_3 \cdot 2H_2O$ (402 mg, 1.5 mmol) and NaN_3 (162.5 mg, 2.5 mmol) in 4.5 mL of MeCN at -20 °C under N_2. The reaction was complete in 5 min. Work up as described above followed by flash chromatography of the residue on silica gel (25:1 hexane-EtOAc) gave 71.9 mg (87.5%) of an inseparable 3:1 mixture of **12a** and **13a**. The data are identical to those previously reported.[12]

***trans*- and *cis*-1,2-Diazidocyclooctane (12b, 13b).** Cyclooctene (0.072 mL, 0.55 mmol) and TFA (0.45 mL) were added to a suspension of $Mn(OAc)_3 \cdot 2H_2O$ (402 mg, 1.5 mmol) and NaN_3 (162.5 mg, 2.5 mmol) in 4.5 mL of MeCN at -20 °C under N_2. The reaction was complete in 5 min. Work up as described above followed by flash chromatography of the residue on silica gel (25:1 hexane-EtOAc) gave 82.2 mg (74%) of an inseparable 5:1 mixture of **12b** and **13b**: ^1H NMR 3.75 (m, 0.16 × 2, **13b**), 3.50 (m, 0.83 × 2, **12b**), 1.35-2.00 (m, 12); ^{13}C NMR (**12b**) 66.6, 29.3, 25.6, 24.7; (**13b**) 63.4, 28.1, 26.4, 23.5; IR (neat) 2930, 2859, 2096.

[1R-(1α,2α,5α)]-2-Azido-2-azidomethyl-6,6-dimethylbicyclo-[3.1.1]-heptane (16a). (1S)-(-)-β-Pinene (0.159 mL, 1.0 mmol) and TFA (0.30 mL) were added to a suspension of $Mn(OAc)_3 \cdot 2H_2O$ (804 mg, 3.0 mmol) and NaN_3 (325 mg, 5.0 mmol) in 9.7 mL of MeCN at -20 °C under N_2. The reaction was warmed up to 25 °C and stirred for 3.5 h. Work up as described above followed by flash chromatography of the residue on silica gel (50:1 hexane-EtOAc) gave 191 mg (87%) of **16a**: ^1H NMR 3.43 (s, 2), 2.36 (m, 1), 2.23 (dd, 1, J = 4.9, 6.2), 2.02-1.78 (m, 5), 1.42 (d, 1, J = 10.4), 1.29 (s, 3), 0.99 (s, 3); ^{13}C NMR 69.4, 59.9, 47.1, 40.2, 38.4, 28.2, 27.5, 25.1, 24.9, 23.3; IR (neat) 2925, 2106. The 2D NOSEY spectrum shows a cross peak between the CH_2N_3 at δ 3.43 and the CH_3 at δ 0.99 establishing the stereochemistry.

[1R-(1α,2α,5α)]-2-Amino-7,7-dimethyl-2-bicyclo[3.1.1]heptaneethanamine (16b). Pd/C (5%, 23 mg) was added to a solution of 191 mg of **16a** in 5 mL of EtOH. The reaction mixture was stirred overnight under 1 atm of H_2 and filtered through celite, which was washed with CH_2Cl_2. The combined filtrates were concentrated under reduced pressure. Flash chromatography of the residue on silica gel (4% Et_3N in 1:1 CH_2Cl_2-CH_3OH) gave 100 mg (59.5%) of **16b**: ^1H NMR 2.69 (d, 1, J = 13.0), 2.64 (d, 1, J = 13.0), 2.23 (m, 1), 1.98-1.72 (m, 9), 1.52 (m, 1), 1.32 (d, 1, J = 10.3), 1.24 (s, 3), 0.98 (s, 3); ^{13}C NMR 56.9, 52.3, 51.1, 41.2, 38.7, 28.6, 28.0, 27.9, 25.2, 23.9; IR (neat) 3399, 2911.

2-Azido-2-cyclohexenone (18). Cyclohexenone (0.048 mL, 0.5 mmol) and TFA (0.45 mL) were added to a suspension of $Mn(OAc)_3 \cdot 2H_2O$ (402 mg, 1.5 mmol) and NaN_3 (162.5 mg, 2.5 mmol) in 4.5 mL of MeCN at -20 °C under N_2. The reaction was warmed up to 25 °C and stirred overnight. Work up as described above followed by flash chromatography of the residue on silica gel (4:1 hexane-EtOAc) gave 42 mg (31%) of **18**: ^1H NMR 6.44 (t, 1, J = 4.6), 2.54 (t, 2, J = 6.6), 2.44 (m, 2), 2.02 (m, 2); ^{13}C NMR 194.0, 135.2, 132.8, 38.3, 25.1, 22.6; IR (neat) 2110, 1682, 1620. The data are identical to those previously reported.[15]

3-Azidocyclooctene (20). TFA (0.20 mL) was added to a suspension of cyclooctene (0.065 mL, 0.5 mmol), $Mn(OAc)_3 \cdot 2H_2O$ (536 mg, 2.0 mmol) and $Cu(OAc)_2$ (91 mg, 0.5 mmol) in 5 mL of acetic acid at 25 °C under N_2. NaN_3 (65 mg, 1.0 mmol) dissolved in 5 mL of acetic acid was then added by a syringe pump over 1.5 h. The reaction mixture was stirred at 25 °C for 1 h and treated with saturated $NaHSO_3$ solution. Flash chromatography of the residue on silica gel

(25:1 hexane-EtOAc) gave 49 mg (65%) of **20** followed by 13 mg (13%) of a 1:1 mixture of **21a**, **21b** and a trace of **12b**.

Data for **20**: ^{1}H NMR 5.77 (dddd, 1, J = 1.5, 8.1, 9.7, 10.6), 5.48 (dd, 1, J = 7.7, 10.6), 4.35 (m, 1), 2.18-2.11 (m, 2), 1.91 (m, 1), 1.76-1.36 (m, 7); ^{13}C NMR 131.2, 129.5, 59.3, 35.3, 28.9, 26.4, 25.9, 24.1; IR (neat) 2932, 2858, 2095, 1651.

Data for *trans*-3,4-diazidocyclooctene (**21a**): ^{1}H NMR 5.92 (dddd, 1, J = 1.0, 8.3, 9.6, 10.4), 5.44 (ddd, 1, J = 1.5, 8.2, 10.4), 4.34 (ddd, 1, J = 1.0, 8.2, 9.8), 3.47 (ddd, 1, J = 4.1, 9.8, 10.2), 2.20 (m, 2), 2.00-1.25 (m, 6); ^{13}C NMR 134.3, 127.1, 67.0, 63.2, 30.0, 28.3, 27.6, 22.3.

Data for *cis*-3,4-diazidocyclooctene (**21b**): ^{1}H NMR 5.98 (dddd, 1, J = 1.3, 7.7, 8.9, 10.5), 5.62 (ddd, 1, J = 1.5, 8.1, 10.5), 4.48 (ddd, 1, J = 1.3, 3.1, 8.1), 3.79 (ddd, 1, J = 3.1, 4.0, 9.2), 2.48-1.30 (m, 8); ^{13}C NMR 134.2, 125.3, 66.0, 60.9, 29.8, 28.9, 26.7, 21.4.

Allylic Azide Formation from 1-Octene. TFA (0.20 mL) was added to a suspension of 1-octene (0.078 mL, 0.5 mmol), $Mn(OAc)_3 \cdot 2H_2O$ (536 mg, 2.0 mmol) and $Cu(OAc)_2$ (182 mg, 1.0 mmol) in 5 mL of acetic acid at 25 °C under N_2. NaN_3 (65 mg, 1.0 mmol) dissolved in 5 mL of acetic acid was then added with a syringe pump over 1.5 h. The reaction mixture was stirred at 25 °C for 1 h and treated with saturated $NaHSO_3$ solution. Flash chromatography of the residue on silica gel (25:1 hexane-EtOAc) gave 37 mg (48%) of an inseparable 28:65:7 mixture of **23** , **24E** and **24Z**, followed by 21 mg (22%) **25**. The structures were assigned by comparison to analogous compounds.[18a,b]

Data for 3-azido-1-octene (**23**) were determined from the mixture: ^{1}H NMR 5.74 (ddd, 1, J = 7.7, 10.6, 16.0), 5.264 (dt, 1, J = 16.0, 1.2), 5.256 (dt, 1, J = 10.6, 1.2), 3.80 (dt, 1, J = 7.7, 7.1), 1.6-1.2 (m, 8), 0.89 (t, 3, J = 6.8); ^{13}C NMR 135.9, 117.9, 65.1, 34.2, 31.4, 29.2, 25.4, 14.0; IR (neat, mixture of **23**-**24**) 2929, 2858, 2099.

Data for 1-azido-2*E*-octene (**24E**) were determined from the mixture: ^{1}H NMR 5.76 (m, 1), 5.51 (m, 1), 3.70 (d, 2, J = 6.4), 2.08 (td, 2, J = 7.0, 7.0), 1.6-1.2 (m, 6), 0.89 (t, 3, J = 6.8); ^{13}C NMR 137.3, 122.6, 52.9, 32.2, 31.3, 28.7, 22.5, 14.0.

Partial data for 1-azido-2*Z*-octene (**24z**) were determined from the mixture: ^{1}H NMR 3.80 (d, 2, J = 7.1); ^{13}C NMR 136.4, 121.8, 52.8.

Data for 1,2-diazidooctane (**25**): ^{1}H NMR 3.46 (m, 1), 3.39 (dd, 1, J = 4.0, 11.6), 3.30 (dd, 1, J = 7.4, 11.6), 1.60-1.20 (m, 10), 0.90 (t, 3, J = 7.4); ^{13}C NMR 62.0, 54.8, 31.7, 31.5, 28.9, 25.8, 22.5, 14.0; IR (neat) 2932, 2860, 2103.

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