Preparation of Novel Haloazide Equivalents by Iodine(III)-Promoted Oxidation of Halide Anions

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Received March 17, 1999

Cohalogenation of alkenes constitutes one of the most important classes of reaction used to form a carbon heteroatom bond in a regio-, chemo-, and stereoselective manner.[1] Since the pioneering work of Hassner[2] considerable attention has been given to the haloazidation of the alkenic double bond by using bromine azide **4a** or iodine azide **4b** as active reagent.[3] This method constitutes a very useful procedure for introducing a nitrogen functionality into a carbon skeleton, leading to vinyl azides,[4] amines,[5] and heterocycles,[6] particularly aziridines.[7]

In continuation of studies devoted to ligand transfer reactions from iodine(III) onto halide ions,[8] we investigated the use of the azide group as a mobile ligand. This method would create haloazide-like species under much milder conditions, namely, in an organic solvent, than commonly applied. A two-phase system by the interaction of Br_2 or NBS with NaN_3 in the presence of acid[7,9] is often required for the preparation of bromine azide. Alternatively, the reagent system NBS/$TMSN_3$ in DME/H_2O has been developed.[10] Iodine azide has been generated from sodium azide and iodine chloride in polar solvents.[11] However, as a result of its explosive character, its use has often been hampered.

Thus, (diacetoxyiodo)benzene (**1**) was reacted with tetraethylammonium bromide (**2a**) in dichloromethane at room temperature and presumably gave tetraethylammonium [di(acyloxy)bromate (I)] (**3a**) (Scheme 1).[12] Treatment of this solution with $TMSN_3$ followed by addition of alkenes **7**−**11** led to the corresponding bromoazidation products **12**, **14**, **16**, **18**, and **19** (Table 1). From these observations it is reasonable to assume that either tetraethylammonium [bis(azido)bromate (I)] (**6a**) or bromine azide **4a** is formed under these conditions (Table 1). When tetraethylammonium iodide (**2b**) was employed, the corresponding 1,2-iodo azides **13**, **15**, and **17** were generated instead, again presumably via the iodate(I)

Scheme 1

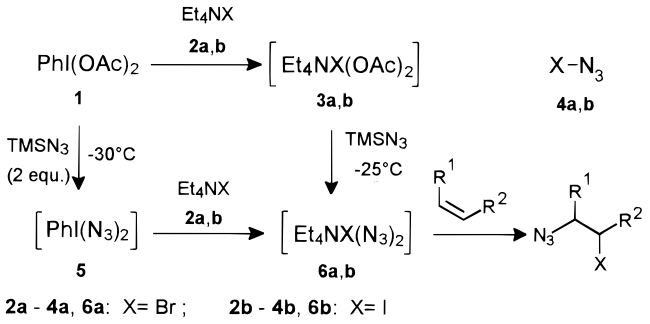
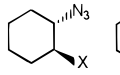
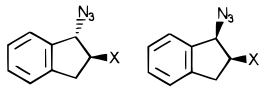
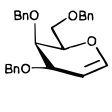
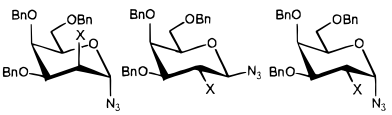
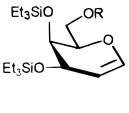
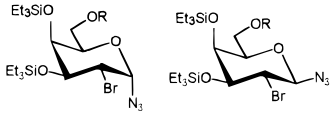


Table 1

	Halide X	Ratio a:b:c[a]	Yield (%)[b]
			
7	Br	*rac*-**12a,b**[c]	>20:1	92
	I	*rac*-**13a,b**[d]	15:1	62
			
8	Br	*rac*-**14a,b**	> 20:1	67
	I	*rac*-**15a,b**	2.5:1	52
			
9	Br	**16a,b,c**	1.3:1.7:1	74
	I	**17a,b,c**[e]	<1:10:0	49
			
10 (R=SiEt$_3$)	Br	**18a,b**	1:1.9	73
11 (R=SiMe$_2$*t*Bu)	Br	**19a,b**	1:1.4	70

[a] Determined from the ^{1}H NMR spectra of the crude product. [b] Total yields of chromatographically purified products. [c] See ref 9a. [d] See ref 2. [e] See ref 17a.

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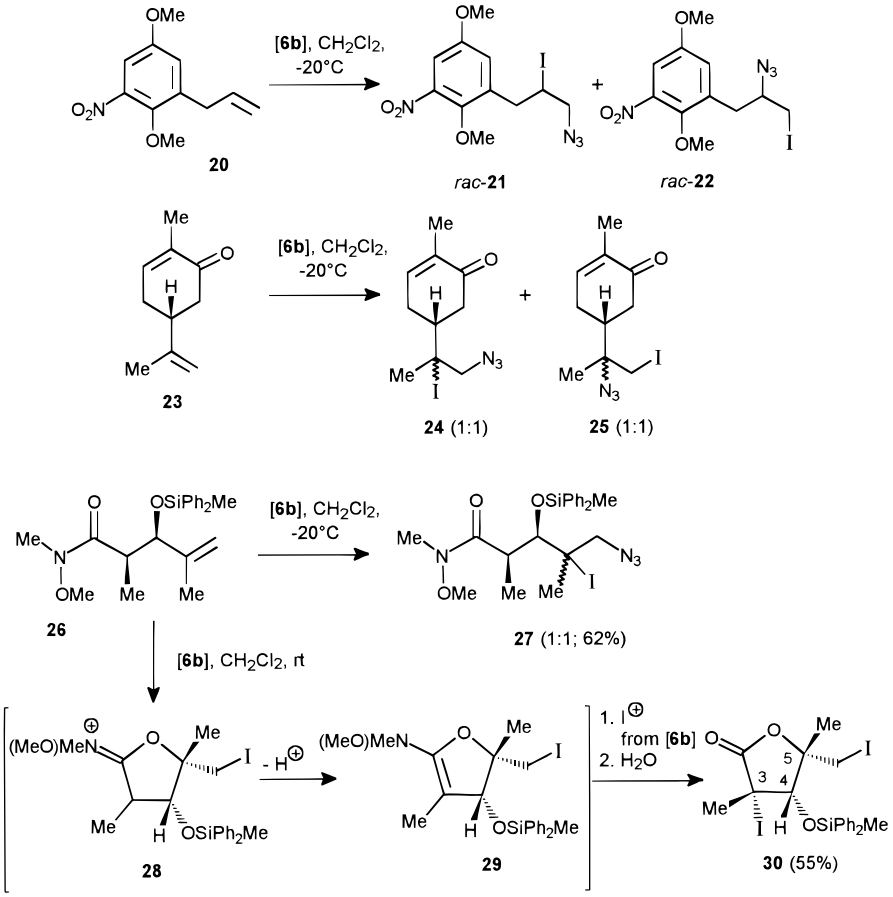
10.1021/jo990478p CCC: $18.00
Published on Web 07/30/1999

Scheme 2



complexes **3b**[13] and **6b**. In this case, iodine azide **4b** may be involved in the addition reaction. The active agent can also be generated by reversing the sequence. In this alternative method, which we found gave yields slightly higher than those of the first route, the hypervalent azidoiodine(III) reagent **5**[14] was formed first, followed by azide transfer onto the tetraalkylammonium halogenides **2a** and **2b**.

In analogy to bromate(I) **6a**, bisazido iodate **6b** promotes azidoiodination of alkenes such as cyclohexene **7** or indene **8**, mostly in a highly *anti*-selective manner (Table 1). Sensitive β-iodo azides **13**[2] and **15** were isolated in good yield. Addition of these haloazide equivalents to carbohydrate-derived cyclic enol ethers **9**−**11** proceeded in a highly regioselective manner, yielding 2-deoxy-2-haloglycosyl azides **16**−**19**. The reduced *anti*-stereoselectivity observed for the addition of the bromate(I) reagent **6a** to glycals **9**−**11** indicates that the intermediate cyclic bromonium is less stable than the corresponding iodonium ion.[3] Thus, the ring oxygen in these pyrans is sufficient to cause ring opening of the intermediate bromonium ion to the oxonium ion. In the case of indene **8**, the aromatic ring exerts a similar enhanced stabilization on the intermediate cation, which results in partial *syn*-addition.

In contrast to the regioselectivity observed in these examples, the nitrophenyl-substituted propene **20**, (*R*)-carvone **23**, and the unsaturated Weinreb amide **26** were preferentially transformed into the *anti*-Markovnikov 1,2-adducts **21** (ratio of regioisomer **21**/**22**, 10:1; 71%), **23** (**24**/**25**, 7.5:1; 78%), and **27** (other regioisomers not found) (Scheme 2).[15] From mechanistic studies it is known that the regioselectivity observed in these examples does not result from a free radical pathway, as is the case for chlorine azide and to some extent bromine azide addition to multiple bonds.[3] In fact, this same phenomenon has been observed before in 1,2-addition reactions to highly hindered terminal alkenes such as 3,3-dimethyl-1-butene.[2,16] Similarly to Hassner and co-workers, we noticed a reduced reaction rate for these alkenes compared to those from Table 1. The oxidation of carvone **23** reveals the pronounced chemoselectivity of the new reagent system, whereas the use of alkene **26** illustrates the remarkable mildness of the halogen-ate complexes by tolerating a wide range of functional groups. At higher temperature, however, the intermediate iodonium ion was opened at the more substituted position in an intramolecular mode, followed by α-iodination of the carbonyl group to quantitatively yield the light-sensitive isomerically pure lactone **30** isolable in 55% yield. From nuclear Overhauser effect (NOE) experiments, the configuration of the three stereogenic centers in **30** was proven. The strong relative NOEs between 4-H and the

(14) Compound **5** can only be generated in situ; its precise structure is unknown: (a) Kirschning, A.; Domann, S.; Dräger, G.; Rose, L. *Synlett* **1995**, 767. (b) Magnus, P.; Lacour, J. *J. Am. Chem. Soc.* **1992**, *114*, 767. (c) Magnus, P.; Lacour, J.; Evans, P. A.; Roe, M. B.; Hulme, C. *J. Am. Chem. Soc.* **1996**, *118*, 3406 and references therein.

(15) The ^{13}C NMR data (in $CDCl_3$) are diagnostic: **21**, 58.2 ppm for CH_2-N_3 and 28.3 ppm for CH−I; **24**, 62.9 ppm for CH_2-N_3 and 57.6 ppm for C−I; **27**, 59.4 and 61.7 ppm for C−I, 62.6 and 62.9 ppm for CH_2-N_3.

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protons of both methyl groups attached to C3 (12.5%) and C5 (13.4%) are a clear proof.

Formation of lactone **30** can be rationalized by assuming that the carbonyl group acts as an intramolecular nucleophile that attacks the primary iodonium ion. After α-deprotonation, the cyclization product **28** is further transformed into **29**. As the iodonium source is employed in excess, a second electrophilic addition initiates the final steps toward **30**.

In summary, we present novel reagent systems that are readily generated in situ from bisazido iodo benzene and tetraalkylammonium halides and that synthetically behave like haloazide equivalents. They can be employed in nonpolar organic solvents and promote azidohalogenation of alkenes, including highly functionalized members, under very mild conditions.

Experimental Section

General Methods. All temperatures quoted are uncorrected. Optical rotations were measured at 581 nm. ^{1}H and ^{13}C NMR spectra were measured with 400 MHz using tetramethylsilane as the internal standard. $CDCl_3$ is the solvent for all NMR experiments except where otherwise stated. All solvents used were of reagent grade and were further dried. Reactions were monitored by TLC on silica gel 60_{P254} and detected either by UV absorption or by staining with H_2SO_4/4-methoxybenzaldehyde in ethanol. Preparative column chromatography was performed on silica gel 60 (230−400 mesh). Glycals **9**−**11** were synthesized according to references.[18,19] Addition products **12**,[9a] **13**,[2] and **17**[17] have been described in detail before. Cyclohexene **7** and indene **8** are commercially available.

General Procedure for the Azidohalogenation of Alkenes. A suspension of $PhI(OAc)_2$ (1 equiv) in dry CH_2Cl_2 (5−10 mL/ mmol) under nitrogen was cooled to −30 °C. $TMSN_3$ (2 equiv) was added, and stirring was continued for 30 min at −30 °C. Then Et_4NI or Et_4NBr (0.75 equiv) was added in one portion, and the color of the solution turned to red-brown. After 15 min of stirring at ambient temperature, alkene (0.25 equiv for alkenes **11**, **20**, and **23**; 0.4 equiv for alkene **26**; and 0.5 equiv for alkenes **7**−**10**) was added. The reaction was monitored by TLC and was terminated by addition of saturated $NaHSO_3$ solution. The aqueous phase was separated and extracted twice with CH_2Cl_2. The combined organic layers were dried ($MgSO_4$) and concentrated in vacuo to afford the crude product which, was purified by flash chromatography. (Note: for the labile iodine azide adducts it is essential to perform workup with $NaHSO_3$ and chromatographic purification as rapid as possible.)

***trans*/*cis*-2-Azido-cyclohexyl Bromide (12a,b).** Cyclohexene **7** (500 mg, 6.08 mmol) was used to prepare the title compound **12a** (1.14 g, 5.6 mmol, 92%) via the general procedure described above. Purification was achieved by column chromatography (petroleum ether/ethyl acetate 80:1). Colorless oil; IR (film) 2099 cm^{-1}; ^{1}H NMR δ 3.87 (ddd, J = 4.2, 9.6, 11.2 Hz, 1H), 3.48 (ddd, J = 4.0, 9.4, 9.4 Hz, 1H), 2.36 (m, 1H), 2.17 (m, 1H), 1.80 (m, 3H), 1.40 (m, 3H); ^{13}C NMR δ 66.9 (d), 55.4 (d), 36.7, 32.2, 26.1, 24.1 (4t). Anal. Calcd for $C_6H_{10}BrN_3$: C, 35.31; H, 4.94; Br, 39.16; N, 20.59. Found C, 35.43; H, 4.83; Br, 39.19; N, 20.43. The *cis*-isomer **12b** was not detected by ^{1}H NMR spectroscopy.

***trans*/*cis*-2-Azido-cyclohexyl Iodide (13a,b).** Cyclohexene **7** (500 mg, 6.08 mmol) was used to prepare the title compounds **13a**,**b** (948 mg, 3.77 mmol, 62%) via the general procedure described above. Purification was achieved by column chromatography (petroleum ether/ethyl acetate 80:1). The ratio for **13a**,**b** was determined to be 15:1 by ^{1}H NMR spectroscopy. Colorless oil **13a**; IR (film) 2097 cm^{-1}; ^{1}H NMR δ 3.96 (ddd, J = 4.0, 10.0, 11.0 Hz, 1H), 3.51 (ddd, J = 4.0, 9.5, 9.5 Hz, 1H), 2.44 (m, 1H), 2.17 (m, 1H), 2.01 (m, 1H), 1.88 (m, 1H), 1.64−1.20 (m, 4H); ^{13}C NMR δ 67.6 (d), 38.8 (t), 33.6 (d), 32.3, 27.5, 24.3 (3t). Anal. Calcd for $C_6H_{10}IN_3$: C, 28.70; H, 4.01; N, 16.74. Found C, 27.96; H, 4.44; N, 15.98.

***trans*-1-Azido-2-bromo-indane (14a).** Indene **8** (500 mg, 4.3 mmol) was used to prepare the title compounds **14a** (687 mg, 2.88 mmol, 67%) via the general procedure described above. Purification was achieved by column chromatography (petroleum ether/ethyl acetate 80:1). Colorless oil; IR (film) 2100 cm^{-1}; ^{1}H NMR δ 7.42−7.20 (m, 4H), 5.04 (d, J = 5.2 Hz, 1H), 4.40 (ddd, J = 5.2, 6.0, 6.8 Hz, 1H), 3.62 (dd, J = 6.8, 16.0 Hz, 1H), 3.26 (dd, J = 6.0, 16.0 Hz, 1H); ^{13}C NMR δ 140.6 (s), 138.5 (s), 129.9 (d), 128.2 (d), 125.3 (d), 125.0 (d), 73.7 (d), 51.6 (d), 41.9 (t). Anal. Calcd for $C_9H_8BrN_3$: C, 45.40; H, 3.39; N, 17.65. Found C, 45.71; H, 3.53; N, 17.77. The *cis*-isomer **14b** was not detected by ^{1}H NMR spectroscopy.

***trans*/*cis*-1-Azido-2-iodo-indane (15a,b).** Indene **8** (500 mg, 4.3 mmol) was used to prepare the title compounds **15a**,**b** (637 mg, 2.24 mmol, 52%) via the general procedure described above. Purification was achieved by column chromatography (petroleum ether/ethyl acetate 80:1). The ratio for **15a**,**b** was determined to be 2.5:1 by ^{1}H NMR spectroscopy.

First fraction (*trans*-**15a**): colorless oil; IR (film) 2104 cm^{-1}; ^{1}H NMR δ 7.49−7.28 (m, 4H), 5.11 (d, J = 5.5 Hz, 1H), 4.36 (ddd, J = 5.5, 6.0, 7.0 Hz, 1H), 3.64 (dd, J = 7.0, 16.0 Hz, 1H), 3.36 (dd, J = 6.0, 16.0 Hz, 1H); ^{13}C NMR δ 142.8 (s), 139.7 (s), 129.1 (d), 128.1 (d), 125.0 (d), 124.9 (d), 70.8 (d), 36.5 (t), 30.9 (d). Anal. Calcd for $C_9H_8IN_3$: C, 37.92; H, 2.83; N, 14.74. Found C, 38.49; H, 3.38; N, 15.11.

Second fraction (*cis*-**15b**): colorless solid, mp 53 °C; IR (film) 2103 cm^{-1}; ^{1}H NMR δ 7.45−7.18 (m, 4H), 5.52 (d, J = 1.6 Hz, 1H), 4.55 (ddd, J = 1.6, 2.0, 6.0 Hz, 1H), 3.40 (dd, J = 6.0, 16.0 Hz, 1H), 2.92 (dd, J = 2.0, 16.0 Hz, 1H); ^{13}C NMR δ 142.7 (s), 138.9 (s), 129.1 (d), 128.1 (d), 125.6 (d), 124.9 (d), 64.2 (d), 37.2 (d), 36.1 (t). Anal. Calcd for $C_9H_8IN_3$: C, 37.92; H, 2.83; N, 14.74. Found C, 37.55; H, 3.06; N, 15.07.

3,4,6-Tri-*O*-benzyl-2-bromo-2-deoxy-α-D-talo-pyranosyl Azide (16a), 3,4,6-Tri-*O*-benzyl-2-bromo-2-deoxy-*β*-D-galacto-pyranosyl Azide (16b), and 3,4,6-Tri-*O*-benzyl-2-bromo-2-deoxy-α-D-galacto-pyranosyl Azide (16c). Glycal **9** (1.2 g, 2.88 mmol) was used to prepare the title compounds **16a**−**c** (1.15 g, 2.13 mmol, 74%) via the general procedure described above. Purification was achieved by column chromatography (petroleum ether/ethyl acetate 20:1). The isomeric ratio (1.3:1.7:1) was determined by ^{1}H NMR spectroscopy.

First fraction (**16c**): colorless oil; $[\alpha]^{22}_D$ = +126.2° (*c* 1.0, $CHCl_3$); IR (film) 2117 cm^{-1}; ^{1}H NMR δ 7.44−7.21 (m, 15H), 5.52 (d, J = 4.0 Hz, 1H), 4.87, 4.73, 4.70, 4.51, 4.49, 4.42 (6d, J = 11.4 and 12.0 Hz, 6H), 4.55 (dd, J = 4.0, 11.0 Hz, 1H), 4.14 (br t, J = 6.0, 6.0 Hz, 1H), 3.94 (dd, J = 1.0, 2.6 Hz, 1H), 3.77 (dd, J = 2.6, 11.0 Hz, 1H), 3.55 (d, J = 6.0 Hz, 2H); ^{13}C NMR δ 138.4−127.8 (Ph), 90.6 (d), 78.3 (d), 74.7 (d), 71.9 (d), 75.1 (t), 73.6 (t), 73.2 (t), 68.3 (t), 64.6 (d). Anal. Calcd for $C_{27}H_{28}O_4BrN_3$: C, 60.23; H, 5.24; N, 7.80; Br, 14.84. Found C, 60.55; H, 5.11; N, 8.01; Br, 14.07.

Second fraction (**16a**): colorless oil; $[\alpha]^{27}_D$ = +36.2° (*c* 1.0, $CHCl_3$); IR (film) 2116 (cm^{-1}); ^{1}H NMR δ 7.24−7.08 (m, 15H), 5.36 (d, J = 4.0 Hz, 1H), 4.82, 4.43, 4.40, 4.33, 4.26, 4.25 (6d, J = 11.2 and 12.0 Hz, 6H), 4.21 (dt, J = 2.8, 6.0, 6.0 Hz, 1H), 3.83 (d, J = 6.0 Hz, 2H), 3.70 (dd, J = 3.6, 4.0 Hz, 1H), 3.54 (dd, J = 2.8, 2.8 Hz, 1H), 3.50 (dd, J = 2.8, 3.6 Hz, 1H); ^{13}C NMR δ 138.5−127.6 (Ph), 89.1 (d), 74.3 (d), 73.7 (d), 73.5 (d), 73.3, 72.1, 72.0 (t), 67.9 (t), 46.8 (d). Anal. Calcd for $C_{27}H_{28}O_4BrN_3$: C, 60.23; H, 5.24; N, 7.80; Br, 14.84. Found: C, 60.31; H, 5.30; N, 7.77; Br, 14.41.

Third fraction **(16b)**: colorless solid, mp 94 °C; $[\alpha]^{20}_D$ = +6.7° (*c* 1.02, $CHCl_3$); IR (KBr) 2119 (cm^{-1}); ^{1}H NMR δ 7.42−7.22 (m, 15H), 4.75 (d, J = 9.6 Hz, 1H), 4.86, 4.71, 4.69, 4.55, 4.46, 4.43 (6d, J = 11.4 and 12.0 Hz, 6H), 4.12 (dd, J = 9.6, 10.6 Hz, 1H), 3.89 (br d, J = 2.8 Hz, 1H), 3.69 (br dd, J = 5.6, 7.0 Hz, 1H), 3.60 (dd, J = 5.6, 9.2 Hz, 1H), 3.57 (dd, J = 7.0, 9.2 Hz, 1H), 3.55 (dd, J = 3.0, 10.6 Hz, 1H); ^{13}C NMR δ 138.0−127.8 (Ph),

(17) In their study of the reaction of glycal **9** and iodoazide, generated by Hassner's procedure (ref 11), Lafont and Descotes observed pronounced α-selectivity: (a) Lafont, D.; Descotes, G. *Carbohydr. Res.* **1987**, *166*, 195−209. (b) Lafont, D.; Guilloux, P.; Descotes, G. *Carbohydr. Res.* **1989**, *193*, 61−73.

(18) Iselin, B.; Reichstein, T. *Helv. Chim. Acta* **1944**, *27*, 1146.

(19) Kirschning, A. *J. Org. Chem.* **1995**, *60*, 1228−1232.

91.0 (d), 82.6 (d), 76.0 (d), 73.1 (d), 74.8 (t), 73.7 (t), 73.2 (t), 68.2 (t), 51.8 (d). Anal. Calcd for $C_{27}H_{28}O_4BrN_3$: C, 60.23; H, 5.24; N, 7.80; Br, 14.84. Found: C, 60.25; H, 5.26; N, 7.81; Br, 14.20.

3,4,6-Tri-*O*-benzyl-1,2-dideoxy-2-iodo-α-D-talo-pyranosyl Azide (17a) and 3,4,6-Tri-*O*-benzyl-1,2-dideoxy-2-iodo-β-D-galacto-pyranosyl Azide (17b). Glycal **9** (250 mg, 0.62 mmol) was used to prepare the title compounds **17a**,**b** (174 mg, 0.30 mmol, 49%) via the general procedure described above. Purification was achieved by column chromatography (petroleum ether/ethyl acetate 8:1). Spectroscopic and analytical data were in accordance with those listed in ref 17. The isomeric ratio (<1:10) was determined by ^{1}H NMR spectroscopy.

2-Bromo-2-deoxy-3,4,6-tri-*O*-(triethylsilyl)-α-D-galacto-pyranosyl Azide (18a) and 2-Bromo-2-deoxy-3,4,6-tri-*O*-(triethylsilyl)-β-D-galacto-pyranosyl Azide (18b). Glycal **10** (1.7 g, 3.48 mmol) was used to prepare the title compounds **18a**,**b** (1.55 g, 2.54 mmol, 73%) via the general procedure described above. Purification was achieved by column chromatography (petroleum ether/ethyl acetate 200:1). The isomeric ratio (1:1.9) was determined by ^{1}H NMR spectroscopy.

First fraction (**18a**): colorless oil; $[\alpha]^{22}_D = +132.9°$ (*c* 1.08, $CHCl_3$); IR (film) 2116 (cm^{-1}); ^{1}H NMR (C_6D_6) δ 5.20 (d, J = 4.0 Hz, 1H), 4.57 (dd, J = 4.0, 10.4 Hz, 1H), 4.21 (d, J = 2.0 Hz, 1H), 4.12 (dd, J = 2.0, 10.4 Hz, 1H), 4.10 (m, 1H), 3.97 (dd, J = 7.2, 10.0 Hz, 1H), 3.88 (dd, J = 6.0, 10.0 Hz, 1H), 1.19−1.04 (m, 27H), 0.88−0.78 (m, 12H), 0.71−0.63 (m, 6H); ^{13}C NMR (C_6D_6) δ 91.1 (d), 75.1 (d), 72.9 (d), 72.0 (d), 61.7 (t), 51.7 (d), 7.2, 6.9 (q), 5.7, 5.6, 4.8 (t). Anal. Calcd for $C_{24}H_{52}BrN_3O_4Si_3$: C, 47.19; H, 8.58; N, 6.88; Br, 13.08. Found: C, 47.21; H, 8.56; N, 6.71; Br, 13.12.

Second fraction (**18b**): colorless oil; $[\alpha]^{23}_D = +12.8°$ (*c* 1.01, $CHCl_3$); IR (film) 2115 (cm^{-1}); ^{1}H NMR (C_6D_6) δ 4.35 (d, J = 8.8 Hz, 1H), 4.28 (dd, J = 8.8, 10.0 Hz, 1H), 4.01 (d, J = 2.0 Hz, 1H), 3.87 (dd, J = 7.2, 10.0 Hz, 1-H), 3.80 (dd, J = 5.6, 10.0 Hz, 1H), 3.55 (dd, J = 2.0, 10.0 Hz, 1H), 3.32 (dd, J = 5.6, 7.2 Hz, 1H), 1.03−0.85 (m, 27H), 0.75−0.43 (m, 18H); ^{13}C NMR (C_6D_6) δ 91.1 (d), 78.1(d), 76.7 (d), 71.9 (d), 61.6 (t), 54.2 (d), 7.2, 7.1, 7.0 (q), 5.7, 5.5, 4.8 (t). Anal. Calcd for $C_{24}H_{52}BrN_3O_4Si_3$: C, 47.19; H, 8.58; N, 6.88; Br, 13.08. Found: C, 47.14; H, 8.67; N, 6.50; Br, 13.23.

2-Bromo-6-*O*-(*tert*-butyldimethylsilyl)-2-deoxy-3,4-di-*O*-(triethylsilyl)-α-D-galacto-pyranosyl Azide (19a) and 2-Bromo-6-*O*-(*tert*-butyldimethylsilyl)-2-deoxy-3,4-di-*O*-(triethylsilyl)-β-D-galacto-pyranosyl Azide (19b). Glycal **11** (366 mg, 0.75 mmol) was used to prepare the title compounds **19a**,**b** (320 mg, 0.52 mmol, 70%) via the general procedure described above. Purification was achieved by column chromatography (petroleum ether/ethyl acetate 100:1). The isomeric ratio (1:1.4) was determined by ^{1}H NMR spectroscopy.

First fraction (**19a**): oil; ^{1}H NMR δ 5.49 (d, J = 3.8 Hz, 1H), 4.36 (dd, J = 3.8, 10.2 Hz, 1H), 3.99 (br s, 1H), 3.86 (dd, J = 2.2, 10.2 Hz, 1H), 3.85 (dt, J = 1.0, 6.2 Hz, 1H), 3.69 (dd, J = 6.2, 10.0 Hz, 1H), 3.65 (dd, J = 6.2, 10.0 Hz, 1H), 0.99 (t, J = 8.0 Hz, 9H), 0.96 (t, J = 8.0 Hz, 9H), 0.89 (s, 9H), 0.75−0.61 (m, 12H), 0.07 (s, 3H), 0.06 (s 3H); ^{13}C NMR δ 90.7 (d), 74.8, (d), 71.5 (d), 72.4 (d), 61.6 (t), 51.2 (d), 25.8 (q), 18.2 (s), 6.92 (q), 6.89 (q), 5.2 [t), 5.1 (t), −5.3 (q), −5.4 (q). Anal. Calcd for $C_{24}H_{52}BrN_3O_4Si_3$: C, 47.19; H, 8.58; N, 6.88; Br, 13.08. Found: C, 47.35; H, 8.77; N, 6.59; Br, 13.20.

Second fraction (**19b**): oil; ^{1}H NMR δ 4.68 (d, J = 9.6 Hz, 1H), 3.97 (dd, J = 9.6, 9.6 Hz, 1H), 3.93 (d, J = 2.3 Hz, 1H), 3.73 (dd, J = 7.1, 10.1 Hz, 1H), 3.69 (dd, J = 6.0, 10.1 Hz, 1H), 3.64 (dd, J = 2.3, 9.6 Hz, 1H), 3.46 (br t, J = 6.2 Hz, 1H), 0.98 (t, J = 8.0 Hz, 9H), 0.96 (t, J = 8.0 Hz, 9H), 0.88 (s, 9H), 0.78−0.56 (m, 12H), 0.07 (s, 6H); ^{13}C NMR δ 91.0 (d), 78.0 (d), 76.3 (d), 71.3 (d), 61.3 (t), 54.0 (d), 25.8 (q), 18.2 (s), 6.9 (q), 5.2 (t), 5.1 (t), −5.3 (q), −5.4 (q). Anal. Calcd for $C_{24}H_{52}BrN_3O_4Si_3$: C, 47.19; H, 8.58; N, 6.88; Br, 13.08. Found: C, 47.08; H, 8.70; N, 6.51; Br, 13.11.

1,4-Dimethoxy-2-nitro-6-[3'-(1'-azido-2'-iodo)propane] (21) and 1,4-Dimethoxy-2-nitro-6-[3'-(2'-azido-1'-iodo)propane] (22). Alkene **20** (167 mg, 0.75 mmol) was used to prepare the title compounds **21** and **22** (208 mg, 0.53 mmol, 71%) via the general procedure described above. Purification was achieved by column chromatography (petroleum ether/ethyl acetate 20:1). The regiomeric ratio (10:1) was determined by ^{1}H NMR spectroscopy.

First fraction (**21**): oil, IR (film) 2111.0 (cm^{-1}); ^{1}H NMR δ 7.28 (d, J = 3.6 Hz, 1H), 6.99 (d, J = 3.6 Hz, 1H), 4.38 (dddd, J = 5.6, 6.2, 6.2, 8.8 Hz, 1H), 3.85 (s, 3H), 3.82 (s, 3H), 3.76 (dd, J = 5.6, 13.0 Hz, 1H), 3.63 (dd, J = 6.2, 13.0 Hz, 1H), 3.37 (dd, J = 6.2, 14.3 Hz, 1H), 3.12 (dd, J = 8.8, 14.3 Hz, 1H); ^{13}C NMR δ 154.9, 145.6, 143.8, 135.9 (s), 122.3, 108.5 (d), 62.6 (q), 58.2 (t), 56.0 (q), 38.8 (t), 28.3 (t). Anal. Calcd for $C_{11}H_{13}O_4N_4I$: C, 33.69; H, 3.34; N, 14.28. Found: C, 33.79; H, 3.34; N, 14.22.

Second fraction (**22**): oil, IR (film) 2105.6 (cm^{-1}); ^{1}H NMR δ 7.30 (d, J = 3.2 Hz, 1H), 7.09 (d, J = 3.2 Hz, 1H), 3.89 (s, 3H), 3.84 (s, 3H), 3.85−3.68 (m, 1H), 3.33 (dd, J = 5.4, 10.7 Hz, 1H), 3.26 (dd, J = 5.7, 10.7 Hz, 1H), 3.10 (dd, J = 5.6, 13.8 Hz, 1H), 2.84 (dd, J = 8.0, 13.8 Hz, 1H); ^{13}C NMR δ: 154.9, 145.6, 143.8, 133.4 (s), 122.4, 108.5 (d), 62.7 (q), 61.8 (t), 55.9 (q), 35.5 (t); 7.8 (t).

(2'*RS*,5*R*)-5-[2'-(1'-Azido-2'-iodo)propyl]-2-methyl-cyclohex-2-en-1-one (24) and (2'*RS*,5*R*)-5-[2'-(2'-Azido-1'-iodo)-propyl]-2-methyl-cyclohex-2-en-1-one (25). (*R*)-Carvone **23** (112 mg, 0.75 mmol) was used to prepare the title compounds **24** and **25** (186 mg, 0.58 mmol, 78%) via the general procedure described above. Purification was achieved by column chromatography (petroleum ether/ethyl acetate 20:1). The regiomeric ratio (7.5:1) was determined by ^{1}H NMR spectroscopy.

First fraction (**24**, 2 diastereomers 1:1): yellow oil; IR (film) 2103.9 (cm^{-1}); ^{1}H NMR δ 6.75 (m, 1H), 3.84 (m, 2H), 2.67−2.20 (m, 4H), 2.10 (s, 3H), 1.84−1.74 (m, 3H), 1.59−1.48 (m, 1H); ^{13}C NMR δ 198.1, 197.9 (s), 143.4, 143.4 (d), 135.4, 135.3 (s), 62.9 (t), 57.6 (s), 44.0, 43.9 (d), 42.9, 42.2, 30.6, 29.9 (t), 30.8, 30.6 (q), 15.5 (q). Anal. Calcd for $C_{10}H_{14}IN_3O$: C, 37.63; H, 4.42; N, 13.17. Found: C, 37.39; H, 4.24; N, 13.77.

Second fraction (**25**, 2 diastereomers 1:1): yellow oil; IR (film) 2105.6 (cm^{-1}); ^{1}H NMR δ 6.70 (m, 1H), 3.33 (s, 2H), 2.55 (m, 5H), 1.74, 1.46 (2 s, 6H); ^{13}C NMR δ 198.3, 198.2 (s), 143.8, 143.5 (t), 135.4, 135.2 (s), 63.2, 63.2 (s), 41.9, 41.8 (t), 38.9, 38.4, 26.9, 26.2 (t), 21.1, 21.0 (q), 15.5 (q), 13.1 (t). Anal. Calcd for $C_{10}H_{14}IN_3O$: C, 37.63; H, 4.42; N, 13.17. Found: C, 37.81; H, 4.19; N, 13.66.

(2*R*,3*R*,4*RS*)-5-Azido-3-(diphenylmethylsiloxy)-4-iodo-*N*-methoxy-*N*,2,4-trimethyl-pentyl Amide (27). Alkene **26** (100 mg, 0.26 mmol) was used to prepare the title compound **27** (87 mg, 0.16 mmol, 62%) via the general procedure described above. Purification was achieved by column chromatography (petroleum ether/ethyl acetate 1:1). The isomeric ratio (1:1) was determined by ^{1}H NMR spectroscopy.

First fraction: brown oil; $[\alpha]^{23}_D = -5.3°$ (*c* 1.0, $CHCl_3$); IR (film) 2105 (cm^{-1}); ^{1}H NMR δ 7.8−7.2 (m, 10H), 4.20 (d, J = 4.4 Hz, 1H), 3.77 (s, 3H), 3.48 (dq, J = 4.4, 7.2 Hz, 1H), 3.40 (s, 2H), 3.17 (s, 3H), 1.81 (s, 3H), 1.12 (d, J = 7.2 Hz, 3H), 0.85 (s, 3H); ^{13}C NMR δ= 175.4 (s), 136.4, 135.9 (s), 134.3−127.3 (d), 76.3 (d), 62.6 (t), 61.6 (q), 59.4 (s), 40.8 (t), 32.6 (q), 28.0 (q), 15.0 (q), −2.4 (q). LRMS (ESI) *m*/*z* 574.9 (M + $Na^{+\cdot}$).

Second fraction: brown oil; $[\alpha]^{23}_D = -25.6°$ (*c* 1.765, $CHCl_3$); IR (film) 2103 (cm^{-1}); ^{1}H NMR δ 7.73−7.32 (m, 10H), 3.75 (s, 3H), 3.56 (d, J = 12.0 Hz, 1H), 3.43 (d, J = 7.2 Hz, 1H), 3.37 (m, 1H), 3.29 (d, J = 12.0 Hz, 1H), 1.74 (s, 3H), 1.08 (d, J = 7.6 Hz, 3H), 0.84 (s, 3H); ^{13}C NMR δ 177.0 (s), 136.2, 136.1 (s), 134.6−127.8 (d), 76.1 (d), 63.0 (t), 61.7 (q), (s), 42.1 (t), 32.6 (q), 28.4 (q), 16.1 (q), −2.8 (q). LRMS (ESI) *m*/*z* 574.9 (M + $Na^{+\cdot}$).

(3*R*,4*R*,5*R*)-3-Iodo-5-iodomethyl-4-(diphenylmethylsilyl-oxy)-dihydro-furan-2-one (30). To a solution of **6b** [generated from 167 mg (0.52 mmol) of $PhI(OAc)_2$, 120 mg (1 mmol) of $TMSN_3$, and 100 mg (0.39 mmol) of Et_4NI] was added alkene **26** (50 mg, 0.13 mmol), and stirring was continued for 2 h at room temperature. Quantitative formation of the title compound **30** was monitored by TLC (petroleum ether/ethyl acetate 3:1; R_f = 0.57). The reaction mixture was rapidly hydrolyzed at 0 °C with saturated $NaHCO_3$. Use of aqueous NH_4Cl, $NaHSO_3$, or $Na_2S_2O_3$ solutions led to complete decomposition of **30**. Extraction of the aqueous phase with CH_2Cl_2 (3×), drying ($MgSO_4$) of the combined washings, and concentration under reduced pressure afforded an oil. Finally, purification was achieved by column chromatography (petroleum ether/ethyl acetate 15:1) and afforded the title compound **30** (42 mg, 0.07 mmol, 55%). Brown oil; $[\alpha]^{23}_D = +8.9°$ (*c* 0.975, $CHCl_3$); IR (film) 1777, 1428, 1379,

1257, 1122, 1086, 1228, 961, 883, 836, 793, 739, 723, 699 (cm^{-1}); ^1H NMR δ 7.72−7.33 (m, 12H), 4.27 (dd, J = 0.8, 11.6 Hz, 1H), 3.30 (d, J = 11.6 Hz, 1H), 3.24 (s, 1H), 1.81 (s, 3H), 1.26 (d, J = 0.8 Hz, 3H), 0.79 (s, 3H); ^{13}C NMR δ 173.1 (s), 134.6, 134.5, 130.9, 130.8, 128.3, 128.2 (t), 133.9, 133.8 (s), 83.2 (s), 81.0 (t), 38.3 (s), 30.2 (q), 28.6 (q), 8.9 (t), −2.0 (q).

Acknowledgment. We thank the Deutschen Akademischen Austauschdienst for a fellowship for Md.A.H. Financial support by the Fonds der Chemischen Industrie is gratefully acknowledged.

JO990478P

Additions and Corrections

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Eric D. Soli, Amy S. Manoso, Michael C. Patterson, Philip DeShong,* David A. Favor, Ralph Hirschmann, and Amos B. Smith, III. Azide and Cyanide Displacements via Hypervalent Silicate Intermediates.

Page 3171. Reference 17 should be a citation to the studies of glycosyl azides from the Györgydeák group at Lajos Kossuth University, Debrecen, Hungary reported in: Györgydeák, Z.; Szilágyi, L.; Paulsen, H. *J. Carbohydr. Chem.* **1993**, *12*, 139−163. The paper cited in ref 17 in the manuscript should have been included in ref 18 instead.

We apologize for having failed to include this citation.

JO9940042

10.021/jo9940042
Published on Web 07/23/1999