Molecular Iodine-Catalyzed Highly Stereoselective Synthesis of Sugar Acetylenes

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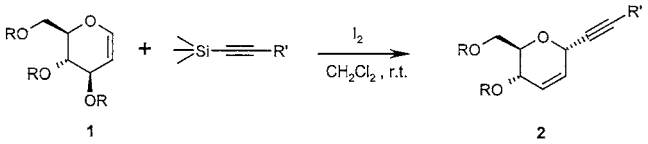
Abstract: D-Glycals react smoothly with alkynylsilanes in the presence of a catalytic amount of molecular iodine under mild and convenient reaction conditions to afford the corresponding alkynyl sugars in excellent yields with high α-selectivity.

Key words: molecular iodine, alkynylsilanes, *C*-glycosides, sugar acetylenes

C-Glycosidation is of great significance in the synthesis of optically active compounds, since it allows the introduction of carbon chains into sugar chirons and the use of sugar nuclei as a chiral pool as well as a carbon source.[1] *C*-Glycosides are versatile chiral building blocks for the synthesis of many biologically interesting natural products such as palytoxin, spongistatin, halichondrin etc.[2] They are potential inhibitors of carbohydrate processing enzymes and are stable analogs of glycans involved in important intra- and inter-cellular processes.[3] In particular, sugar acetylenes are attractive due to the presence of a triple bond that can be easily transformed into other chiral molecules and carbohydrate analogues.[4] In addition, sugar acetylenes are useful precursors as chiral templates in the synthesis of many natural products such as ciguatoxin and tautomycin, etc.[5] Lewis acids such as boron trifluoride, tin tetrachloride and titanium tetrachloride are employed as promoters in the *C*-alkynylation of glycals with alkynylsilanes.[6] However, many of these reagents are corrosive, moisture sensitive and are required in stoichiometric amounts. Therefore, the developments of simple and inexpensive reagents, which are more efficient and provide convenient procedures with improved yields, are well appreciated. In addition, there is an advantage in developing a catalytic process for the synthesis of alkynyl sugars. Owing to its unique catalytic properties, iodine has been extensively used for a plethora of organic transformations including glycosidation reactions.[7] However, there are no reports on the iodine catalyzed *C*-alkynylation of glycals with alkynylsilanes.

In continuation of our interest on the catalytic applications of molecular iodine for various organic transformations,[8] we describe herein another remarkable catalytic activity of iodine in the *C*-glycosidation of glycals with alkynylsilanes (Scheme 1).



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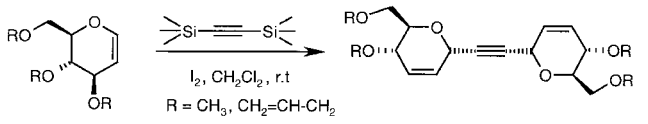
Scheme 1

Thus, treatment of 3,4,6-tri-*O*-acetyl-D-glucal with phenyl (trimethylsilyl) acetylene in the presence of 5 mol% of iodine at ambient temperature resulted in the formation of alkynyl *C*-glycoside in 90% yield. Only the α-anomer was obtained in each reaction, the structure of which was confirmed by ^{1}H NMR spectrum of crude product. In a similar fashion, various derivatives of D-glucal reacted smoothly with a range of alkynyltrimethylsilanes to give the corresponding alkynyl *C*-pseudoglycals in excellent yields (Table 1). However, the reaction of pentose sugars such as 3,4-*O*-di-acetyl-D-xylal with phenyl(trimethylsilyl)acetylene gave the corresponding phenylethynyl-D-pseudoxylal in good yield with 1,4-*anti* selectivity (entry g). Furthermore, the treatment of 3,4,6-tri-*O*-allyl or methyl derivatives of D-glucal with bis(trimethylsilyl)acetylene under the influence of elemental iodine afforded the corresponding *bis*-glycosilated alkynes in high yields (Scheme 2).



1 2

Scheme 2

Similarly, di-*O*-acetyl derivative of L-rhamnal also reacted smoothly with bis(trimethylsilyl)acetylene to afford *bis*-glycosilated alkyne derivative in 89% yield (entry k). However, in case of 3-trimethylsilyl-2-propyn-1-ol, *O*-glycopyranoside was obtained in high yield with high α–selectivity (entry l). All products were characterized by ^{1}H, ^{13}C NMR, IR spectra and also by comparison with authentic compounds.[4,6] There are several advantages in the use of iodine as catalyst for this transformation, which include high yields of products, cleaner reaction profiles, high α-selectivity and easy availability of the catalyst at low cost. In addition, this method does not require any additives or stringent reaction conditions and no precautions need to be taken to exclude moisture from the reaction

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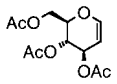
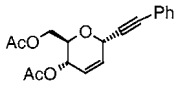
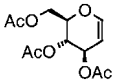
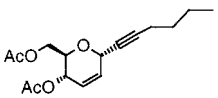
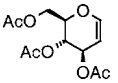
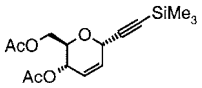
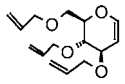
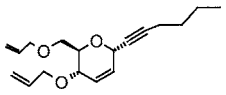
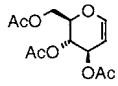
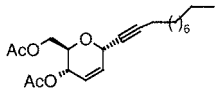
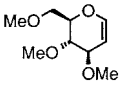
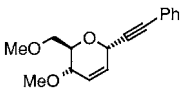
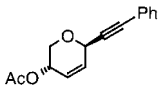
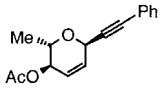
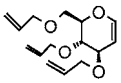
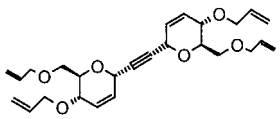
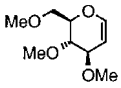
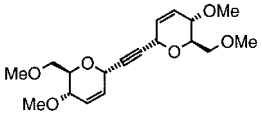
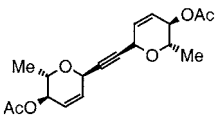
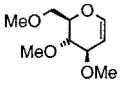
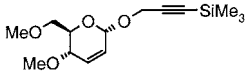
Table 1 Iodine-Catalyzed Preparation of Sugar Acetylenes from D-Glycals

Entry	Substrate (1)	Product[a] (2)	Time (h)	Yields (%)[b]
a			3.0	90
b			3.5	87
c			3.0	85
d			2.5	83
e			3.0	90
f			2.5	87
g			3.0	90[c]
h			4.0	92
i			3.5	85
j			3.0	87
k			3.5	89
l			2.5	90

[a] All products were characterized by IR, ^1H, ^{13}C NMR and mass spectroscopy.
[b] Isolated and unoptimized yields.
[c] Anti-selectivity was obtained in the case of pentose sugars.

medium. The experimental procedure is simple and convenient affording the products in excellent yields within a short period. In addition, the reaction conditions are amenable to scale-up. Among various catalysts such as scandium triflate, ytterbium triflate, cerium triflate and indium triflate employed for this transformation, molecular iodine was found to be a more effective catalyst in terms of yields and reaction rates. Furthermore, the products were obtained in low to moderate yields (45–60%) along with deacetylated glycals when TMSI was employed as a catalyst for this reaction. Thus, this method is advanced with respect to the existing procedures for the preparation of alkynyl sugars where Lewis acids are employed as promoters. The scope and generality of this process is illustrated with respect to various glycals and alkynylsilanes. The results are presented in the Table 1.

In summary, this paper describes a simple and convenient method for the synthesis of alkynyl *C*-pseudoglycals from glycals and alkynylsilanes using a catalytic amount of iodine under very mild reaction conditions. This method provides high yields of alkynyl *C*-glycosides with high anomeric selectivity, which makes it a useful process for the synthesis of sugar acetylenes of synthetic importance.

Melting points were recorded on Buchi R-535 apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer FT-IR 240-c spectrophotometer using KBr optics. ^{1}H NMR spectra were recorded on Gemini-200 spectrometer in $CDCl_3$ using TMS as internal standard. Mass spectra were recorded on a Finnigan MAT 1020 mass spectrometer operating at 70 eV. CHN analyses were recorded on a Vario EL analyzer. The optical rotations were measured on a Jasco Dip 360 Digital polarimeter.

Acetylene Derivatives; General Procedure

A mixture of 3,4,6-tri-*O*-acetyl-D-glucal (5 mmol), trimethylsilyl acetylene (5 mmol) and iodine (5 mol%) in CH_2Cl_2 (10 mL) was stirred at r.t. After complete conversion, as indicated by TLC, the reaction mixture was diluted with H_2O (10 mL) and extracted with CH_2Cl_2 (2 × 15 mL). The organic layers were dried over anhyd Na_2SO_4 and purified by column chromatography on silica gel (Merck, 100–200 mesh, EtOAc–hexane, 1:9) to afford pure sugar acetylene derivative. Spectroscopic data for selected compounds:

2a

α-Isomer; liquid; $[\alpha]_D^{25}$ –105.7 (*c* 1.0, $CHCl_3$).

IR (KBr): 3024, 2125, 1745, 1577, 1402, 1219, 1092, 768, 666 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 2.03 (s, 6 H), 4.10 (ddd, 1 H, *J* = 3.0, 6.5, 8.9 Hz), 4.20 (ddd, 2 H, *J* = 3.0, 6.5, 12.0 Hz), 5.15 (br s, 1 H), 5.25 (dd, 1 H, *J* = 2.2, 8.9 Hz), 5.78 (dd, 1 H, *J* = 2.0, 10.7 Hz), 5.90 (dt, 1 H, *J* = 2.1, 10.7 Hz), 7.20–7.30 (m, 3 H), 7.38–7.40 (m, 2 H).

^{13}C NMR (proton decoupled, $CDCl_3$): δ = 20.6, 20.9, 63.0, 64.4, 64.8, 70.0, 84.7, 86.6, 122.2, 125.4, 128.2, 128.6, 129.1, 131.7, 170.1, 170.7.

MS (FAB): *m*/*z* = 314 [M$^+$], 267, 231, 137, 123, 109, 77.

2b

α-Isomer; liquid; $[\alpha]_D^{25}$ –82.5 (*c* 3.5, $CHCl_3$).

IR (neat): 2967, 2217, 1731, 1463, 1372, 1238, 1046, 758 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 0.95 (t, 3 H, *J* = 6.2 Hz), 1.30–1.50 (m, 4 H), 2.01 (s, 6 H), 2.12 (t, 2 H, *J* = 6.3 Hz), 4.0 (ddd, 1 H, *J* = 3.0, 6.5, 9.0 Hz), 4.20 (ddd, 2 H, *J* = 3.0, 6.5, 12.5 Hz), 4.95 (br s, 1 H), 5.25 (dd, 1 H, *J* = 1.9, 9.0 Hz), 5.60 (dd, 1 H, *J* = 1.9, 10.3 Hz), 5.82 (dt, 1 H, *J* = 2.0, 10.3 Hz).

^{13}C NMR (Proton decoupled, $CDCl_3$): δ = 13.2, 20.6, 21.2, 21.8, 29.3, 31.7, 21.8, 63.1, 64.1, 65.0, 69.7, 76.0, 77.61, 87.4, 124.6, 130.0, 170.1, 170.7.

MS (EI): *m*/*z* = 280 [M$^+$], 239, 193, 151, 108, 69, 43.

2c

α-Isomer; liquid; $[\alpha]_D^{25}$ –80.9 (*c* 1, $CHCl_3$).

IR (neat): 2985, 2214, 1731, 1634, 1425, 1373, 1237, 1060, 758 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 0. 05 (s, 9 H), 1.98 (s, 6 H) 3.80 (ddd, 1 H, *J* = 3.0, 6.3, 9.0 Hz), 4.08 (ddd, 2 H, *J* = 3.0, 6.3, 11.8 Hz), 4.75 (br s, 1 H), 5.0 (dt, 1 H, *J* = 2.0, 9.0 Hz), 5.55 (dd, 1 H, *J* = 2.0, 10.1 Hz), 5.65 (dt, 1 H, *J* = 2.1, 10.1 Hz).

^{13}C NMR (proton decoupled, $CDCl_3$): δ = 0.2, 21.0, 21.4, 63.8, 65.1, 65.3, 70.1, 91.2, 101.1, 125.7, 128.2, 170.6, 170.9.

MS (EI): *m*/*z* = 310 [M$^+$], 239, 214, 109.

2d

α-Isomer; liquid; $[\alpha]_D^{25}$ –35.6 (*c* 1.5, $CHCl_3$).

IR (KBr): 2936, 2856, 2195, 1630, 1614, 1215, 1025, 752 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 0.98 (t, 3 H, *J* = 6.8 Hz), 1.35–1.60 (m, 4 H), 2.80 (t, 2 H, *J* = 6.5 Hz), 3.65 (dd, 2 H, *J* = 3.5, 12.0 Hz), 3.85 (m, 1 H), 4.10 (m, 2 H), 4.15 (m, 2 H), 4.30 (dq, 1 H, *J* = 2.5, 9.0 Hz), 5.10–5.25 (m, 4 H), 5.35 (br s, 1 H), 5.60 (dd, 1 H, *J* = 2.0, 10.2 Hz), 5.80–6.0 (m, 2 H), 6.10 (dt, 1 H, *J* = 2.5, 10.2 Hz).

^{13}C NMR ($CDCl_3$, proton decoupled): δ = 13.2, 18.4, 20.6, 20.8, 29.8, 31.7, 58.1, 68.4, 69.1, 69.9, 70.0, 72.2, 75.2, 93.4, 116.7, 117.1, 126.9, 128.8, 134.2.

MS (EI): *m*/z = 290 [M$^+$], 234, 210, 109, 41.

2e

α-Isomer; liquid; $[\alpha]_D^{25}$ –87.5 (*c* 3.5, $CHCl_3$).

IR (KBr): 2927, 2856, 2214, 1744, 1673, 1461, 1371, 1228, 1048, 771 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 0.9 (t, 3 H, *J* = 6.3 Hz), 1.30–1.40 (m, 14 H), 2.03 (s, 6 H), 2.10 (t, 2 H, *J* = 6.5 Hz), 4.10 (ddd, 1 H, *J* = 3.3, 6.5, 9.0 Hz), 4.20 (ddd, 2 H, *J* = 3.3, 6.5, 11.7 Hz), 4.90 (d, 1 H, *J* = 1.4 Hz), 5.20 (dd, 1 H, *J* = 2.2, 9.0 Hz), 5.70 (dd, 1 H, *J* = 1.4, 10.7 Hz), 5.83 (dt, 1 H, *J* = 2.2, 10.7 Hz).

^{13}C NMR (proton decoupled, $CDCl_3$): δ = 13.9, 18.6, 20.6, 20.8, 22.5, 28.4, 28.7, 28.9, 29.1, 29.3, 31.7, 63.0, 64.1, 64.9, 69.6, 75.8, 87.6, 124.6, 130.0, 170.0, 170.6.

MS (FAB): *m*/*z* = 364 [M$^+$], 239, 193, 151, 108, 69, 43.

2f

α-Isomer; solid; mp 155–156 °C; $[\alpha]_D^{25}$ –39.6 (*c* 1.2, $CHCl_3$).

IR (neat): 2931, 2212, 1604, 1463, 1238, 1061, 758 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 3.42 (s, 6 H), 3.70 (dd, 2 H, *J* = 3.0, 9.0 Hz), 3.98 (m, 2 H), 5.10 (br s, 1 H), 5.92 (dd, 1 H, *J* = 2.0, 10.0 Hz), 6.02 (dt, 1 H, *J* = 2.2, 10.2 Hz), 7.31(m, 3 H), 7.40 (m, 2 H).

^{13}C NMR (proton decoupled, $CDCl_3$): δ = 29.2, 31.6, 56.4, 59.2, 69.0, 71.3, 71.6, 91.2, 91.8, 122.2, 125.3, 127.4, 128.2, 129.4, 131.6, 169.8, 170.2.

MS (EI): *m*/*z* = 258 [M^+], 182, 156, 142, 103, 77, 63.

2g

α-Isomer; liquid; $[\alpha]_D^{25}$ 64.8 (*c* = 1.1, $CHCl_3$).

IR (KBr): 3033, 2211, 1733, 1601, 1405, 1219, 1097, 778 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 2.10 (s, 3 H), 3.90 (d, 1 H, *J* = 13.0 Hz), 4.20 (dd, 1H *J* = 3.0, 13.0 Hz), 4.90 (br s, 1 H), 5.10 (br s, 1 H), 5.90 (dd, 1 H, *J* = 4.4, 10.2 Hz), 6.10 (dd, 1 H, *J* = 3.6, 10.2 Hz), 7.25–7.30 (m, 3 H), 7.38–7.40 (m, 2H).

^{13}C NMR (proton decoupled, $CDCl_3$): δ = 20.9, 63.3, 63.8, 64.1, 84.6, 96.0, 122.5, 128.1, 128.5, 131.2, 131.7, 132.0, 133.4, 133.2, 170.3.

MS (EI): *m*/*z* = 242 [M^+], 165, 156, 142, 77, 63.

2h

α-Isomer; viscous liquid; $[\alpha]_D^{25}$ –25.5 (*c* 1.1, $CHCl_3$).

IR (neat): 3025, 2219, 1745, 1636, 1370, 1054, 759 cm^{-1}.

^{1}H NMR ($CDCl_3$) δ = 1.25 (d, 3 H, *J* = 6.0 Hz), 2.10 (s, 3 H), 4.10 (m, 1 H), 5.01 (dd, 1 H, *J* = 1.5, 9.5 Hz), 5.37 (br s, 1 H), 5.78 (dd, 1 H, *J* = 1.2, 10.6 Hz), 5.98 (dt, 1 H, *J* = 1.5, 10.6 Hz), 7.25–7.30 (m, 3 H), 7.38–7.40 (m, 2 H).

^{13}C NMR (proton decoupled, $CDCl_3$): δ = 17.4, 20.4, 64.6, 70.2, 84.6, 96.0, 122.4, 125.4, 128.2, 128.6, 129.1, 132.1, 170.5, 170.8.

MS (EI): *m*/*z* = 256 [M^+], 179, 155, 140, 77, 63.

2i

α-Isomer; liquid; $[\alpha]_D^{25}$ –62.6 (*c* 1.0, $CHCl_3$).

IR (neat): 3005, 2195, 1630, 1614, 1412, 1220, 1060, 754 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 3.65 (m, 4 H), 3.85 (m, 2 H), 3.98–4.17 (m, 8 H), 4.30 (dd, 2 H, *J* = 2.1, 9.0 Hz), 4.95 (br s, 2 H), 5.15–5.20 (m, 4 H), 5.25–5.35 (m, 4 H), 5.75 (dd, 2 H, *J* = 1.8, 10.3 Hz), 5.85–5.95 (m, 4 H), 6.12 (dt, 2 H, *J* = 2.1, 10.3 Hz).

^{13}C NMR (proton decoupled, $CDCl_3$): δ = 22.4, 27.9, 58.2, 68.4, 68.9, 68.9, 69.4, 69.9, 70.0, 70.1, 72.2, 72.3, 75.2, 76.5, 93.8, 94.8, 116.7, 116.8, 116.9, 117.0, 117.1, 117.3, 226.4, 128.4, 128.8, 134.2, 134.5.

MS (FAB): *m*/*z* = 442 [M^+], 411, 383, 289, 265, 209, 166, 151, 137, 109, 97, 81, 69, 55.

2j

α-Isomer; liquid; $[\alpha]_D^{25}$ 35.5 (*c* 1.2, $CHCl_3$).

IR (neat): 2924, 2176, 2853, 1634, 1456, 1314, 848, 765 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 3.40 (s, 12 H), 3.61 (dd, 4 H, *J* = 2.9, 11.0 Hz), 3.75–3.80 (m, 2 H), 3.85 (dd, 2 H, *J* = 1.9, 9.5 Hz), 4.82 (br s, 2 H), 5.75 (dd, 2 H, *J* = 1.6, 9.9 Hz), 6.05 (dt, 2 H, *J* = 1.9, 9.9 Hz).

^{13}C NMR (proton decoupled, $CDCl_3$): δ = 29.2, 31.6, 56.4, 59.2, 69.0, 71.3, 71.7, 91.2, 101.2, 126.5, 131.6.

MS (FAB): *m*/*z* = 338 [M^+], 279, 181, 158, 137, 109, 81, 69, 43.

2k

α-Isomer; liquid; $[\alpha]_D^{25}$ –40.1 (*c* 1.0, $CHCl_3$).

IR (KBr): 3033, 2211, 1733, 1601, 1405, 1219, 1097, 778 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 1.23 (d, 6 H, *J* = 6.0 Hz), 2.08 (s, 6 H), 3.96 (dq, 2 H, *J* = 6.0, 9.2 Hz), 5.07 (dd, 2 H, *J* = 1.8, 9.2 Hz), 5.37 (br s, 2 H), 5.79 (dd, 2 H, *J* = 1.5, 10.2 Hz), 5.88 (dd, 2 H, *J* = 1.8, 10.2 Hz).

^{13}C NMR (proton decoupled, $CDCl_3$): δ = 17.4, 20.4, 64.6, 70.2, 124.5, 127.1, 129.3, 169.8.

MS (FAB): *m*/*z* = 334 [M^+], 277, 221, 191, 155, 137, 109, 81, 69, 55.

2l

Liquid; $[\alpha]_D^{25}$ 141.9 (*c* 3.0, $CHCl_3$).

IR (neat): 2950, 2123, 1652, 1438, 1370, 1225, 1108, 1040, 920 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 0.15 (s, 9 H), 3.40 (s, 6 H), 3.58 (dd, 2 H, *J* = 3.0, 12.0 Hz), 3.70 (dt, 1 H, *J* = 3.0, 9.0 Hz), 3.85 (dd, 1 H, *J* = 2.5, 9.0 Hz), 4.20 (s, 2 H), 5.15 (br s, 1 H), 5.70 (dt, 1 H, *J* = 2.5, 10.5 Hz), 6.05 (dd, 1 H, *J* = 2.2, 10.5 Hz).

^{13}C NMR ($CDCl_3$, proton decoupled): δ = –0.2, 29.6, 31.8, 55.6, 56.4, 59.2, 69.0, 71.3, 71.7, 91.2, 92.8, 101.2, 126.1, 130.6.

MS (FAB): *m*/*z* = 284 [M^+], 211, 161, 142, 100, 82, 69, 55, 43.

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