Iodophosphoryloxylation of Carbon−Carbon Multibonds and Its Application to Glycals

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Iodophosphoryloxylation of carbon−carbon multibonds was attempted. Alkynes and cyclohexene were converted to the corresponding 1,2-iodophosphoryloxylated compounds in moderate to good yields with a trivalent iodine compound/iodine system, while glucal gave mainly the corresponding iodohydrin compound in this system. However, 2-deoxy-2-iodoglycosyl diphenylphosphinates were obtained from the corresponding glycals with a diphenylphosphinic acid/iodine/potassium carbonate system in good yields. Moreover, triethylborane smoothly reduced 2-deoxy-2-iodoglycosyl diphenylphosphinates to 2-deoxyglycosyl diphenylphosphinates in a 1,4-cyclohexadiene solvent.

Introduction

Introduction of a halogen and a nucleophile to carbon−carbon multiple bonds at the same time is called a cohalogenation reaction, and extensive study has been carried out.[1] In the intramolecular cohalogenation reactions, especially, iodine-induced intramolecular cyclizaton reactions are very valuable for the construction of cyclic compounds.[2] In the intermolecular cohalogenation reaction, alkoxide, carboxylate, amide, and azide anions are often used as nucleophiles to introduce hydroxyl and amino groups;[1c] however, the study on use of phosphoric acids as nucleophiles in cohalogenation reactions is limited.[3] The introduction of a phosphate group in sugar compounds is very important in view of biological activity, enzymatic inhibitors, and *O*- and *C*-glycosidation.[3b,4] In fact, phosphorylated sugars are key intermediates in the metabolism of monosaccharides as well as in biosynthesis of complex oligosaccharides. Both the phosphonate and *C*-glycoside partial structures are effective mimics for the corresponding moieties in naturally occurring sugar phosphates. Thus, we planned to carry out the iodophosphoryloxylation of carbon−carbon multibonds.

Results and Discussion

1. Iodophosphoryloxylation of Alkynes and Alkene. Recently, the study and synthetic use of organohypervalent iodine compounds have been widely carried out,[5] especially, organotrivalent iodine compounds having sulfonyloxy groups, which are often used as oxidants because of their powerful oxidation ability.[5,6] We have already reported the iodotosyloxylation of alkynes with 1-(arenesulfonyloxy)benziodoxolones,[7] and we confirmed that a trivalent iodine compound/iodine system was one of the best methods for the cohalogenation reaction of alkynes. Therefore, we planned to perform iodophosphoryloxylation of alkynes with a trivalent iodine compounds/iodine system and to explore their synthetic application. To date, study on the synthetic use of organotrivalent iodine compounds having phosphoryloxy groups has been quite limited.[8] Thus, {[bis(phenoxy)phosphoryloxy](hydroxy)iodo}benzene (**1**) and [(diphenylphosphoryloxy)-(hydroxy)iodo]benzene (**2**) were prepared, and the iodophosphoryloxylation of alkynes and alkene was studied. The results with alkynes are shown in Table 1.

Totally, iodane **1** gave the iodophosphoryloxylated alkenes in better yields than the use of iodane **2**, and the yields of alkenes **4** and **5** depend on the electron density of the carbon−carbon triple bond. Thus, diphenylacetylene (**3a**) was iodophosphoryloxylated with iodane **1** to give the alkene **4a** in moderate yield under conditions A, while iodane **2** gave the iodophosphoryloxylated alkene **5a** in poor yield (entries 1 and 2). When the amount of alkyne **3a** was increased from 1.2 equiv to 5.0 equiv (conditions B), the yield of compound **5a** was increased up to 26% (entry 3). 4-Octyne (**3b**) was converted to the

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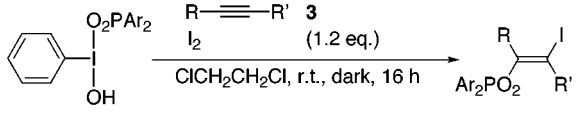
Table 1. Iodophosphoryloxylation of Alkynes 3



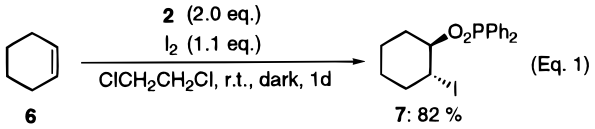
1: Ar = PhO
2: Ar = Ph

4: Ar = PhO
5: Ar = Ph

Entry	Iodane	Alkyne			Conditions[a)]	Product	
		R	R'	3		4 or 5	Yield / %
1	**1**	Ph	Ph	**3a**	A	**4a**	58
2	**2**	Ph	Ph	**3a**	A	**5a**	14
3	**2**	Ph	Ph	**3a**	B	**5a**	26
4	**1**	*n*-Pr	*n*-Pr	**3b**	A	**4b**	84
5	**2**	*n*-Pr	*n*-Pr	**3b**	A	**5b**	86
6	**1**	Ph	Me	**3c**	A	**4c**	85
7	**2**	Ph	Me	**3c**	A	**5c**	67
8	**1**	Ph	H	**3d**	B	**4d**	27
9	**1**	Ph	H	**3d**	C	**4d**	33
10	**1**	*n*-Bu	H	**3e**	A	**4e**	30
11	**1**	*n*-Bu	H	**3e**	C	**4e**	79
12	**2**	*n*-Bu	H	**3e**	B	**5e**	29

a) A: alkyne **3** (1.2 eq.), solv. 2.5 mL; B: alkyne **3** (5.0 eq.), solv. 2.5 mL; C: alkyne **3** (5.0 eq.), solv. 5.0 mL.

corresponding adducts **4b** and **5b** with iodanes **1** and **2**, effectively (entries 4 and 5). Terminal alkynes **3d** and **3e** gave the corresponding adducts in poor yields. Iodophosphoryloxylation of ethyl propiolate with iodanes **1** and **2** did not proceed, because of the low electron density of the carbon−carbon triple bond. Here, iodophosphoryloxylation of alkyne **3b** with a phosphonic acid/iodine system did not proceed at all. Cyclohexene (**6**) was converted to the corresponding adduct **7** in 82% yield with an iodane **2**/iodine system (eq 1) while a phosphinic acid/iodine/potassium carbonate system gave the adduct **7** in only 26% yield under the best conditions. Thus, the reactive intermediate of these cohalogenation reactions was a phosphonyl hypoiodite species, which is formed by the reaction of iodane **2** and iodine. The formed phosphonyl hypoiodite species adds to alkynes or cyclohexene via ionic pathway.

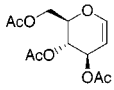


(Eq. 1)

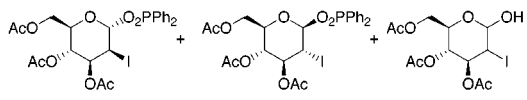
6 **7**: 82 %

2. Iodophosphoryloxylation of Glycals. Introduction of iodine and a nucleofugal anion, such as acetate and phosphate, to glycals is very important, because these glycosyl esters are excellent glycosyl donors and, moreover, precursors of 2-deoxysugars.[9] Thus today, many iodoacetoxylation methods for carbon−carbon double bonds including glycals have been developed.[10] However, iodophosphoryloxylation methods are quite limited, because their preparation is difficult.[4c] Therefore, we planned to develop a convenient iodophosphoryloxylation method with glycals based on the above results. At first, a trivalent iodine compound/iodine system to obtain 2-deoxy-2-iodoglycosyl phosphinate was employed, and the results are shown in Table 2.

Table 2. Iodophosphoryloxylation of Glucal 8a with Trivalent Iodine Compound/Iodine System



8A



9A-α **9A-β** **10A**

Entry	"I"	Conditions[a)]	Yields / %			Recovery / %
			9A-α	9A-β	10A	
1	I_2	A	0	0	72	0
2	I_2	B	20	4	56	0
3	$[Ph_3PCH_3]^+ I^-$	C	6	2	22	39
4	$[Ph_3PCH_3]^+ I^-$	D	10	5	13	59
5	$[Ph_3PCH_3]^+ I^-$	E	24	5	10	49

a) A: 4.0 eq., $ClCH_2CH_2Cl$ (2.5 mL), 5 d; B: 2.0 eq., $CHCl_3$ (5 mL), 5 d, Ph_2PO_2H (2.0 eq.); C: 2.0 eq., $ClCH_2CH_2Cl$ (2.5 mL), 3 d; D: 4.0 eq., $ClCH_2CH_2Cl$ (2.5 mL), 6 d; E: 4.0 eq., $CHCl_3$ (10 mL), 6 d, Ph_2PO_2H (4.0 eq.).

However, iodohydrin compound **10A** was obtained in 72% yield, instead of the corresponding glycosyl ester **9A** (entry 1).[11] Probably, here the iodophosphoryloxylation of glucal occurred, and the subsequent hydrolysis by the hydroxy group derived from iodane **2** at the reactive anomeric position in the sugar compound occurred to give iodohydrin **10** because of the phosphinate anion as a good leaving group. Then, diphenylphosphinic acid was added to the reaction mixture (entry 2), and the corresponding adduct **9A** was obtained in 24% yield (**9A**-α and **9A**-*β*). However, the iodohydrin compound **10A** was still the main product. In entries 3−5, phosphonium iodide was used as the iodine source. This cohalogenation system was reported by Kirschning et al. and the reactive intermediate was a halogen-ate(I) complex.[12] As a result, in a trivalent iodine compound/phosphonium iodide system, prolonged reaction time was required and the yield of **9A** could not be improved. Then, iodophosphoryloxylation of glycals with a phosphinic acid/iodine system was carried out (Table 3).

In entries 1−3, the corresponding iodophosphoryloxylated adducts **9A** were obtained in moderate yields together with glucal **8A** in 10−40% yields. Under the best conditions, the corresponding adduct **9A** was obtained in

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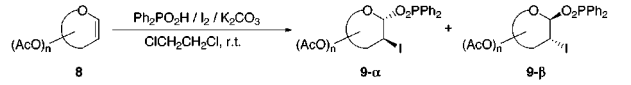
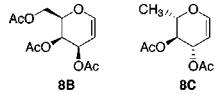
Table 3. Iodophosphoryloxylation of Glycal 8 with Diphenylphosphinic Acid/Iodine System

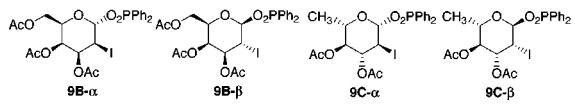


8 9-α 9-β

Entry	Glycal[a]	Conditions				Products[b]		Yields / %	
		Ph_2PO_2H / eq.	I_2 / eq.	K_2CO_3 / eq.	Time / d	9-α	9-β	9-α	9-β
1	**8A**	1.1	1.1	1.1	3	**9A-α**	**9A-β**	34	5
2	**8A**	2.0	1.1	2.0	3	**9A-α**	**9A-β**	36	6
3	**8A**	4.0	2.0	4.0	3	**9A-α**	**9A-β**	57	9
4	**8A**	8.0	4.0	8.0	3	**9A-α**	**9A-β**	74	9
5	**8A**	8.0	4.0	8.0	1	**9A-α**	**9A-β**	71	22
6	**8B**	8.0	4.0	8.0	1	**9B-α**	**9B-β**	82	4
7	**8C**	8.0	4.0	8.0	1	**9C-α**	**9C-β**	4	19
8	**8C**	8.0	4.0	8.0	1	**9C-α**	**9C-β**	10	59[c]

a) 

8B **8C**

b) 

9B-α **9B-β** **9C-α** **9C-β**

c) Na_2SO_4 was added.

Table 4. ^{1}H NMR Spectra of Compounds 9

Adduct	9A-α	9A-β	9B-α	9B-β	9C-α	9C-β
δ / ppm[a]	6.12	5.63	6.24	5.63	5.57	6.08
Pattern	dd	dd	d	dd	dd	d
J / Hz	7.3, 1.4	9.2, 8.3	7.0	9.3, 8.7	8.9, 8.0	7.4
NOE[b]	X	O (14 %)	?	O (9 %)	O (15 %)	X

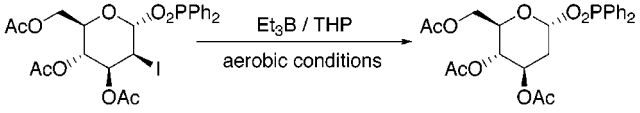
a) anomeric proton

b) 1-H↔5-H; X: not observed; O: observed; ?: not identified

93% yield in the presence of K_2CO_3 (8 equiv) finally (entry 5). Galactal (**8B**) and 6-deoxy-L-glucal (**8C**) were converted to the corresponding glycosyl phosphinates under the same conditions. Galactal (**8B**) was iodophosphoryloxylated in good yield (entry 6), and compound **9C** was obtained in 69% yield in the presence of sodium sulfate to keep dry conditions (entry 8). In the absence of sodium sulfate, glycosyl ester **9C** was formed in only 23% yield (entry 7), and an iodohydrin compound was observed by ^{1}H NMR. The NIS (*N*-iodosuccinimide)/diphenylphosphinic acid system gave the corresponding ester **9A** in moderate yield (**9A-**α: 37%, **9A-**β: 12%). The stereochemistry of adducts **9** was established based on Niggemann's report[4c,13] and ^{1}H NMR experiment (Table 4).

Conversion of glycosyl ester **9A-**α to 2-deoxymannosyl diphenylphosphinate (**11A-**α) was attempted. Hydride reagents such as lithium aluminiun hydride were often used to reduce the iodide.[14] However, hydride reduction was not favorable to obtain compound **11A-**α, because the compound **9A-**α has two good leaving groups; one is an iodine atom and the other is a phosphinate group. Thus, we used a radical reduction method to obtain 2-deoxymannosyl diphenylphosphinate (**11A-**α). At first, treatment of compound **9A-**α with diphenylsilane/triethylborane system was attempted.[15] Diphenylsilane and glycosyl ester **9A-**α were stirred in THF solution, and white precipitates were formed. The compound **9A-**α reacted with diphenylsilane alone before the addition of triethylborane to form diphenylphosphinic acid and a complex mixture. Then, radical reduction was carried out by triethylborane alone (Table 5).

Table 5. Reduction of Compound 9A-α to Compound 11A-α



9A-α **11A-α**

Entry	Conditions				Yields / %	
	Et_3B / eq.	Solvent	Temp. / °C	Time / h	11A-α	8A
1	12	THF	r.t.	2	44	54
2	12	THF	0	2	53	45
3	12	THF	0	2	51[a]	43
4	12	THF	-30~-20	2	51	41
5	12		0	2	73[b]	0
6	12 x 2		0	4	88	0

a) K_2CO_3 (4.0 eq.) was added.

b) Starting material **9A-**α was recovered in 21 % yield.

In entry 1, the corresponding reduced compound **11A-**α was obtained in 44% yield together with glucal **8A** in 54% yield. We speculated two plausible formation mechanisms of glucal: one is Lewis acid and/or proton acid, derived from triethylborane under aerobic conditions, induced elimination of diphenylphosphinic acid from the compound **11A-**α; the other is radical β-elimination of the diphenylphosphoryloxy group from the sugar radical. In entries 2−4, lowering reaction temperature and addition of potassium carbonate did not make any remarkable difference. We thought the formation of glucal **8A** came from the radical β-elimination of 1-(diphenylphosphinyl)-2-deoxy-2-glycosyl radical. Thus, in entries 5 and 6, the solvent was changed from THF to 1,4-cyclohexadiene which is an effective hydrogen donor. Finally, 2-deoxymannosyl diphenylphosphinate (**11A-**α) was obtained in 88% yield, and glucal **8A** did not form at all (entry 6).

Conclusion

Alkynes and cyclohexene were iodophosphoryloxylated with a trivalent iodine compound/iodine system to give the corresponding 1,2-iodophosphoryloxylated compounds in moderate to good yields, while glucal was converted to the corresponding iodohydrin compound under the same conditions. However, 2-deoxy-2-iodoglycosyl diphenylphosphinates were obtained in good yields with a diphenylphosphinic acid/iodine/potassium carbonate system. Triethylborane smoothly reduced 2-deoxy-2-iodoglycosyl diphenylphosphinate to 2-deoxyglycosyl diphenylphosphinate in 1,4-cyclohexadiene solvent.

Experimental Section

General. All iodophosphoryloxylated reactions were performed under an argon atmosphere. ^{1}H NMR spectra were recorded on 400 and 500 MHz spectrometers, and ^{13}C NMR

(13) Niggemann et al. reported that the preparation of (2-iodo-2-deoxy-α-mannopyranosyl)(dibenzyl) phosphate and (2-iodo-2-deoxy-β-glucopyranosyl)(dibenzyl) phosphate, and their chemical shift of anomeric proton [5.92 (dd, J = 5.7, 1.3 Hz, α-manno form) and 5.51 (dd, J = 9.1, 7.4 Hz, β-gluco form)].

(14) Larock, R. C. In *Comprehensive Organic Transformation*; VCH Publisher: New York, 1989; p 18.

(15) (a) Barton, D. H. R.; Jang, D. O.; Jaszberenyi, J. Cs. *Synlett* **1991**, 435. (b) Barton, D. H. R.; Jang, D. O.; Jaszberenyi, J. Cs. *Tetrahedron Lett.* **1991**, *32*, 2569.

spectra were recorded on 100 and 125 MHz spectrometers. Chemical shifts are reported as ppm downfield from tetramethylsilane (TMS) in δ units. *J*-Values are given in hertz. In the ^{13}C NMR spectra, p, s, t, and q means primary, secondary, tertiary, and quaternary. The matrix of mass spectra (FAB) used 3-nitrobenzyl alcohol. Melting points were determined on an electrothermal apparatus in open capillary tubes and are uncorrected. Kieselgel 60 F254 (Merck) was used for TLC, and Wakogel B-5F was used for pTLC.

Materials. Iodanes **1**[8a] and **2**[8e] were prepared by the literature method. Alkynes **3**, aromatics **6**, glycals **8**, and triethylborane (1 M solution in THP) were commercially available.

Iodophosphoryloxylation Reaction of Alkynes. Iodane **1** (235.0 mg, 0.5 mmol) and iodine (152.4 mg, 0.6 mmol) were added to a solution of alkyne **3b** (275.0 mg, 2.5 mmol) in $ClCH_2CH_2Cl$ (2.5 mL) and stirred for 16 h under dark conditions at rt. Then the reaction mixture was poured into saturated aqueous Na_2SO_3 solution and extracted with chloroform (20 mL × 3). The organic layer was dried over Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by preparative TLC on silica gel using hexane: ethyl acetate (8:1) as an eluent. (*E*)-4-Iodo-5-[(diphenoxy)-phosphoryloxy]-4-octene **4b** was obtained in 84% yield (204.1 mg).

(*E*)-1-Iodo-2-[(diphenoxy)phosphoryloxy]stilbene (4a): mp 128−129 °C; IR (KBr) 3060, 1650, 1300, 760 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 6.69 (4H, d, *J* = 8.5 Hz), 7.06−7.40 (12H, m), 7.51 (2H, d, *J* = 8.2 Hz), 7.61−7.64 (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 89.02 (q, J_{C-P} = 10 Hz), 119.77 (t, J_{C-P} = 5 Hz), 125.13 (t), 128.15 (t), 128.23 (t), 128.37 (t), 129.50 (t), 129.70 (t), 130.38 (t), 136.16 (q), 139.88 (q), 145.43 (q, J_{C-P} = 9 Hz), 150.14 (q, J_{C-P} = 9 Hz); MS (FAB) found: $(M + H)^+$ = 555, calcd for $C_{26}H_{21}IO_4P$: M = 555. Anal. Found: C, 56.25; H, 3.74%. Calcd for $C_{26}H_{20}IO_4P$: C, 56.34; H, 3.64%.

(*E*)-4-Iodo-5-[(diphenoxy)phosphoryloxy]-4-octene (4b): oil; IR (neat) 2960, 1650, 1290, 730 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ = 0.77 (3H, t, *J* = 7.3 Hz), 0.90 (3H, t, *J* = 7.3 Hz), 1.45 (2H, sextet, *J* = 7.4 Hz), 1.56 (2H, sextet, *J* = 7.3 Hz), 2.40 (2H, t, *J* = 7.1 Hz), 2.70 (2H, t, *J* = 7.5 Hz), 7.19−7.26 (6H, m), 7.34−7.37 (4H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 12.79 (p), 13.36 (p), 20.07 (s), 22.48 (s), 38.26 (s), 38.97 (s), 95.53 (q, J_{C-P} = 10 Hz), 120.11 (t, J_{C-P} = 5 Hz), 125.59 (t), 129.86 (t), 147.00 (q, J_{C-P} = 10 Hz), 150.50 (q, J_{C-P} = 8 Hz); HRMS (FAB) found: $(M + H)^+$ = 487.0528, calcd for $C_{20}H_{25}IO_4P$: M = 487.0535. Found: C, 49.52; H, 4.83%. Calcd for $C_{20}H_{24}IO_4P$: C, 49.40; H, 4.97%.

(*E*)-1-Phenyl-1-[(diphenoxy)phosphoryloxy]-2-iodo-1-propene (4c): oil; IR (neat) 3060, 1300, 780 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 2.54 (3H, d, *J* = 2.6 Hz), 6.99 (4H, d, *J* = 7.5 Hz), 7.13 (2H, t, *J* = 7.2 Hz), 7.22−7.35 (7H, m), 7.44−7.48 (2H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 27.00 (p), 87.45 (q, J_{C-P} = 10 Hz), 199.93 (t, J_{C-P} = 5 Hz), 125.38 (t), 127.97 (t), 129.34 (t), 129.65 (t), 130.16 (t), 133.63 (q), 136.12 (q), 145.02 (q, J_{C-P} = 9 Hz), 150.29 (q, J_{C-P} = 7 Hz); HRMS (FAB) found: $(M + H)^+$ = 493.0058, calcd for $C_{21}H_{19}IO_4P$: M = 493.0066.

(*E*)-1-Iodo-2-phenyl-2-[(diphenoxy)phosphoryloxy]-1-ethene (4d): oil; IR (neat) 3070, 1300, 760 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 6.61 (1H, d, *J* = 2.6 Hz), 7.12−7.40 (13H, m), 7.58 (2H, dd, *J* = 8.2, 1.9 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 64.77 (t, J_{C-P} = 6 Hz), 120.06 (t, J_{C-P} = 6 Hz), 125.65 (t), 128.13 (t), 128.72 (t), 129.30 (t), 129.86 (t), 129.92 (t), 133.55 (q, J_{C-P} = 5 Hz), 149.72 (q, J_{C-P} = 9 Hz), 150.35 (q, J_{C-P} = 9 Hz); HRMS (FAB) found: $(M + H)^+$ = 478.9910. calcd for $C_{20}H_{17}IO_4P$: M + H = 478.9909.

(*E*)-1-Iodo-2-[(diphenoxy)phosphoryloxy]-1-hexene (4e): oil; IR (neat) 3080, 2960, 1300, 760 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 0.87 (3H, t, *J* = 7.3 Hz), 1.31 (2H, sextet, *J* = 7.6 Hz), 1.44 (2H, quint, *J* = 8.3 Hz), 2.51 (2H, t, *J* = 7.3 Hz), 6.19 (1H, d, *J* = 2.2 Hz), 7.20−7.26 (6H, m), 7.34−7.38 (4H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 13.80 (p), 21.87 (s), 28.02 (s), 33.63 (s, J_{C-P} = 5 Hz), 63.90 (t, J_{C-P} = 6 Hz), 120.06 (t, J_{C-P} = 5 Hz), 125.69 (t), 129.88 (t), 150.35 (q, J_{C-P} = 8 Hz), 153.33 (q, J_{C-P} = 10 Hz); HRMS (FAB) found: $(M + H)^+$ = 459.0213, calcd for $C_{18}H_{21}IO_4P$: M + H = 459.0222.

(*E*)-1-Iodo-2-(diphenylphosphoryloxy)stilbene (5a): mp 117−118 °C; IR (KBr) 3060, 1230, 700 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ = 7.16−7.40 (18H, m, Ar), 7.53 (2H, d, *J* = 6.6 Hz, Ar); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 86.82 (q, J_{C-P} = 7 Hz), 127.66 (t), 127.93 (t), 128.04 (t), 128.23 (t), 129.19(t), 129.60 (t), 130.35 (q), 130.46 (t), 131.50 (t, J_{C-P} = 12 Hz), 131.88 (t, J_{C-P} = 2 Hz), 136.41 (q), 140.72 (q), 146.68 (q, J_{C-P} = 9 Hz), 150.14 (q, J_{C-P} = 9 Hz); MS (FAB) found: $(M + H)^+$ = 523, calcd for $C_{26}H_{21}IO_2P$: M + H = 523. Anal. Found: C, 59.64; H, 3.92%. Calcd for $C_{26}H_{20}IO_2P$: C, 59.79; H, 3.86%.

(*E*)-4-Iodo-5-(diphenylphosphoryloxy)-4-octene (5b): oil; IR (neat) 3060, 2960, 1240, 750 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ = 0.80 (3H, t, *J* = 7.4 Hz), 0.81 (3H, t, *J* = 7.3 Hz), 1.41 (2H, sextet, *J* = 7.4 Hz), 1.51 (2H, sextet, *J* = 7.4 Hz), 2.40 (2H, t, *J* = 7.4 Hz), 2.53 (2H, t, *J* = 7.7 Hz), 7.45−7.50 (4H, m), 7.56 (2H, td, *J* = 7.0, 1.4 Hz), 7.83 (4H, ddd, J_{H-P} = 12.4 Hz, *J* = 8.0, 1.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 13.08 (p), 13.51 (p), 20.36 (s), 22.68 (s), 39.18 (s), 39.65 (s), 94.29 (q, J_{C-P} = 8 Hz), 128.72 (t, J_{C-P} = 13 Hz), 131.59 (t, J_{C-P} = 11 Hz), 131.74 (q, J_{C-P} = 137 Hz), 132.54 (t, J_{C-P} = 3 Hz), 147.71 (q, J_{C-P} = 10 Hz); HRMS (FAB) found: $(M + H)^+$ = 455.0638, calcd for $C_{20}H_{25}IO_2P$: M + H = 455.0637.

(*E*)-1-Phenyl-1-(diphenylphosphoryloxy)-2-iodo-1-propene (5c): mp 128−129 °C; IR (KBr) 3050, 1240, 870 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ = 2.71 (3H, d, *J* = 2.1 Hz), 7.06−7.16 (5H, m), 7.30−7.33 (4H, m), 7.42−7.46 (2H, m), 7.60−7.65 (4H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 27.78 (p), 87.31 (q, J_{C-P} = 6 Hz), 127.55 (t), 128.24 (t, J_{C-P} = 13 Hz), 128.62 (q), 130.01 (t), 130.42 (t), 131.57 (t, J_{C-P} = 10 Hz), 132.10 (t, J_{C-P} = 2 Hz), 137.16 (q), 145.40 (q, J_{C-P} = 10 Hz), 150.29 (q, J_{C-P} = 7 Hz); MS (FAB) found: $(M + H)^+$ = 461, calcd for $C_{21}H_{19}IO_2P$: M + H = 461. Anal. Found: C, 54.84; H, 4.02%. Calcd for $C_{21}H_{18}IO_2P$: C, 54.80; H, 3.94%.

(*E*)-1-Iodo-2-(diphenylphosphoryloxy)-1-hexene (5e): mp 34.5−35.5 °C; IR (KBr) 3080, 2920, 1220, 950 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ = 0.90 (3H, t, *J* = 7.3 Hz), 1.33 (2H, sextet, *J* = 7.5 Hz), 1.53 (2H, quint, *J* = 7.5 Hz), 2.47 (2H, t, *J* = 7.6 Hz), 6.05 (1H, d, *J* = 2.1 Hz), 7.45−7.57 (6H, m), 7.79−7.83 (4H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 13.83 (p), 21.89 (s), 28.31 (s), 34.49 (s, J_{C-P} = 3 Hz), 62.62 (t, J_{C-P} = 6 Hz), 128.60 (t, J_{C-P} = 14 Hz), 130.81 (q, J_{C-P} = 139 Hz), 131.58 (t, J_{C-P} = 10 Hz), 132.53 (t, J_{C-P} = 3 Hz), 153.56 (q, J_{C-P} = 10 Hz); HRMS (FAB) found: $(M + H)^+$ = 427.0297, calcd for $C_{18}H_{21}IO_2P$: M + H = 427.0324.

(2-Iodocyclohexyl) diphenylphosphinate (7): mp 107−108 °C; IR (KBr) 3060, 2950, 1240, 750 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ = 1.34−1.41 (2H, m), 1.55−1.65 (2H, m), 1.77−1.80 (1H, m), 1.93−1.99 (1H, m), 2.31−2.40 (2H, m,), 4.30 (1H, ddd, *J* = 8.6, 8.6, 3.8 Hz), 4.43−4.49 (1H, m), 7.44−7.47 (4H, m), 7.51−7.55 (2H, m), 7.87−7.91 (4H, m); ^{13}C NMR (125 MHz) δ = 22.71 (s), 25.71 (s), 32.44 (s), 33.09 (t, J_{C-P} = 6 Hz), 36.21 (s), 78.65 (t), 128.37 (t, J_{C-P} = 14 Hz), 128.43 (t, J_{C-P} = 14 Hz), 131.69 (t, J_{C-P} = 10 Hz), 131.97 (t, J_{C-P} = 11 Hz), 132.10 (t), 132.15 (q, J_{C-P} = 139 Hz); MS (FAB) found: $(M + H)^+$ = 427, calcd for $C_{18}H_{21}IO_2P$: M + H = 427. Anal. Found: C, 50.70; H, 4.95%. Calcd for $C_{18}H_{20}IO_2P$: C, 50.72; H, 4.73%.

Iodohydroxylation Reaction of Glucal with a Trivalent Iodine Compound/Iodine System. A solution of iodane **2** (876.0 mg, 2.0 mmol) and iodine (508.0 mg, 2.0 mmol) in $ClCH_2CH_2Cl$ (2.5 mL) was stirred for 1 h, and then glucal **8A** (136.0 mg, 0.5 mmol) was added to the solution. The solution was stirred for 5 d under dark conditions at rt. Then the reaction mixture was poured into saturated aqueous Na_2SO_3 solution and extracted with chloroform (20 mL × 3). The organic layer was dried over Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by preparative TLC on silica gel using hexane:ethyl acetate (1:1) as an eluent. Iodohydrin compound **10A** was obtained in 72% yield (149.8 mg).

Iodophosphoryloxylation Reaction of Glucal with a Trivalent Iodine Compound/Phosphonium Iodide System. A solution of iodane **2** (876.0 mg, 2.0 mmol), methyltriphenylphosphonium iodide (808.0 mg, 2.0 mmol), and

diphenylphosphinic acid (436.0 mg, 2.0 mmol) in $CHCl_3$ (10 mL) was stirred for 1 h, and then glucal **8A** (136.0 mg, 0.5 mmol) was added to the solution. The solution was stirred for 6 d under dark conditions at rt. The reaction mixture was poured into saturated aqueous Na_2SO_3 solution and extracted with chloroform (20 mL × 3). The organic layer was dried over Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by preparative TLC on silica gel using hexane:ethyl acetate (1:2) as an eluent. (3,4,6-Tri-*O*-acetyl-2-deoxy-2-iodo-α-D-mannopyranosyl) diphenylphosphinate (**9A-**α) and (3,4,6-tri-*O*-acetyl-2-deoxy-2-iodo-*β*-D-glucopyranosyl) diphenylphosphinate (**9A-***β*) were obtained in 24% (73.9 mg) and 5% (15.4 mg), respectively, together with iodohydrin compound **10A** (20.8 mg, 10%).

Iodophosphoryloxylation Reaction of Glucal with a Diphenylphosphinic Acid/Iodine System. Diphenylphosphinic acid (436.0 mg, 2.0 mmol), iodine (254.0 mg, 1.0 mmol), and potassium carbonate (276.0 mg, 2.0 mmol) were added to a solution of glucal **8A** (68.0 mg, 0.25 mmol) in $ClCH_2CH_2Cl$ (5.0 mL), and the solution was stirred for 1 d at rt. The reaction mixture was poured into saturated aqueous Na_2SO_3 solution and extracted with chloroform (20 mL × 3). The organic layer was dried over Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by preparative TLC on silica gel using hexane:ethyl acetate (1:2) as an eluent. (3,4,6-Tri-*O*-acetyl-2-deoxy-2-iodo-α-D-mannopyranosyl) diphenylphosphinate (**9A-**α) and (3,4,6-tri-*O*-acetyl-2-deoxy-2-iodo-*β*-D-glucopyranosyl) diphenylphosphinate (**9A-***β*) were obtained in 71% (109.3 mg) and 22% (33.9 mg), respectively.

(3,4,6-Tri-*O*-acetyl-2-deoxy-2-iodo-α-D-mannopyranosyl) diphenylphosphinate (9A-α): foam; IR (KBr) 3060, 2920, 1750, 1370, 1230, 730 cm^{-1}; ^1H NMR (500 MHz) δ = 2.05 (3H, s), 2.07 (3H, s), 2.11 (3H, s), 3.82 (1H, dd, J = 13.6, 3.5 Hz), 4.10−4.14 (2H, m), 4.69 (1H, dd, J = 4.3, 1.4 Hz), 4.77 (1H, dd, J = 9.8, 4.3 Hz), 5.47 (1H, t, J = 9.8 Hz), 6.12 (1H, dd, 7.3, 1.4 Hz), 7.47−7.61 (6H, m), 7.78−7.84 (4H, m); ^{13}C NMR (125 MHz) δ = 20.55 (p), 20.64 (p), 20.84 (p), 28.90 (t, J_{C-P} = 5 Hz), 61.40 (s), 66.99 (t), 68.28 (t), 70.93 (t), 96.66 (t, J_{C-P} = 4 Hz), 128.67 (t, J_{C-P} = 13 Hz), 128.83 (t, J_{C-P} = 15 Hz), 130.06 (q, J_{C-P} = 138 Hz), 130.49 (q, J_{C-P} = 135 Hz), 131.35 (t, J_{C-P} = 10 Hz), 131.68 (t, J_{C-P} = 10 Hz), 132.80 (t, J_{C-P} = 7 Hz), 169.24 (q), 169.83 (q), 170.54 (q); HRMS (FAB) found: $(M + H)^+$ = 617.0396, calcd for $C_{24}H_{27}IO_9P$: M + H = 617.0437.

(3,4,6-Tri-*O*-acetyl-2-deoxy-2-iodo-*β*-D-glucopyranosyl) diphenylphosphinate (9A-*β*): mp 126−127 °C (dec); IR (KBr) 3060, 2950, 1750, 1730, 1240, 750 cm^{-1}; ^1H NMR (500 MHz) δ = 1.97 (3H, s), 2.00 (3H, s), 2.08 (3H, s), 3.75 (1H, ddd, J = 10.1, 5.2, 2.3 Hz), 3.92 (1H, dd, J = 12.2, 2.3 Hz), 4.07−4.13 (2H, m), 4.96 (1H, dd, J = 10.1, 9.2 Hz), 5.29 (1H, dd, J = 11.1, 9.1 Hz), 5.63 (1H, dd, 9.2, 8.3 Hz), 7.43−7.58 (6H, m), 7.82−7.86 (4H, m); ^{13}C NMR (125 MHz) δ = 20.52 (p), 20.57 (p), 20.67 (p), 27.56 (t, J_{C-P} = 8 Hz), 61.58 (s), 68.66 (t), 72.53 (t), 75.15 (t), 96.97 (t, J_{C-P} = 6 Hz), 128.21 (t, J_{C-P} = 14 Hz), 128.44 (t, J_{C-P} = 16 Hz), 130.47 (q, J_{C-P} = 139 Hz), 131.08 (q, J_{C-P} = 136 Hz), 131.70 (t, J_{C-P} = 12 Hz,), 131.98 (t, J_{C-P} = 12 Hz), 132.42 (t), 132.61 (t), 169.43 (q), 169.49 (q), 170.34 (q); MS (FAB) found: $(M + H)^+$ = 617, calcd for $C_{24}H_{27}IO_9P$: M + H = 617.

3,4,6-Tri-*O*-acetyl-2-deoxy-2-iodohydrin (10A): oil; IR (neat) 2960, 1740, 1370, 600 cm^{-1}; ^1H NMR (500 MHz) δ = 2.07 (3H, s), 2.10 (3H, s), 2.13 (3H, s), 4.19−4.20 (2H, m), 4.26−4.30 (1H, m), 4.58 (1H, dd, J = 4.4, 1.2 Hz), 4.73 (1H, dd, J = 9.3, 4.4 Hz), 5.39 (1H, t, J = 9.6 Hz), 5.60 (1H, bs); ^{13}C NMR (125 MHz) δ = 20.64 (p), 20.78 (p), 20.92 (p), 30.26 (t), 62.26 (s), 67.65 (t), 68.75 (t), 69.14 (t), 95.82 (t), 169.61 (q), 170.0 (q), 170.01 (q); HRMS (FAB) found: $(M + H)^+$ = 417.0024, calcd for $C_{12}H_{18}IO_8$: M + H = 417.0046.

(3,4,6-Tri-*O*-acetyl-2-deoxy-2-iodo-α-D-talopyranosyl) diphenylphosphinate (9B-α): foam; IR (KBr) 3060, 3000, 1760, 1740, 1370, 1210, 730 cm^{-1}; ^1H NMR (500 MHz) δ = 2.01 (3H, s), 2.08 (3H, s), 2.16 (3H, s), 3.83 (1H, dd, J = 11.2, 6.3 Hz), 4.08 (1H, dd, J = 11.2, 7.3 Hz), 4.44−4.47 (2H, m), 5.00 (1H, t, J = 3.7 Hz), 5.44 (1H, bs), 6.24 (1H, d, J = 7.0 Hz), 7.47−7.61 (6H, m), 7.75−7.85 (4H, m); ^{13}C NMR (125 MHz) δ = 20.37 (t, J_{C-P} = 6 Hz), 20.56 (p), 20.75 (p), 20.85 (p), 61.00 (s), 64.28 (t), 64.58 (t), 68.24 (t), 98.32 (t, J_{C-P} = 5 Hz), 128.66 (t, J_{C-P} = 13 Hz), 128.76 (t, J_{C-P} = 13 Hz), 130.19 (q, J_{C-P} = 139 Hz), 130.29 (q, J_{C-P} = 134 Hz), 131.23 (t, J_{C-P} = 11 Hz), 131.68 (t, J_{C-P} = 11 Hz), 132.73 (t, J_{C-P} = 4 Hz), 132.76 (t, J_{C-P} = 3 Hz), 169.49 (q), 169.88 (q), 170.15 (q); HRMS (FAB) found: $(M + H)^+$ = 617.0386, calcd for $C_{24}H_{27}IO_9P$: M + H = 617.0437.

(3,4,6-Tri-*O*-acetyl-2-deoxy-2-iodo-*β*-D-galactopyranosyl) diphenylphosphinate (9B-*β*): oil; IR (neat) 3060, 2920, 1730, 1360, 750 cm^{-1}; ^1H NMR (500 MHz) δ = 1.94 (3H, s), 2.06 (3H, s), 2.14 (3H, s), 3.47−4.01 (3H, m), 4.24 (1H, dd, J = 11.8, 9.3 Hz), 5.09 (1H, dd, J = 11.6, 3.4 Hz), 5.20 (1H, d, J = 3.1 Hz), 5.63 (1H, dd, J = 9.3, 8.7 Hz), 7.44−7.58 (6H, m), 7.83−7.88 (4H, m); MS (FAB) found: $(M + H)^+$ = 617.

(3,4-Di-*O*-acetyl-2,6-dideoxy-2-iodo-α-L-glucopyranosyl) diphenylphosphinate (9C-α): mp 105−106 °C (dec); IR (KBr) 3060, 2980, 1750, 1380, 1240 and 730 cm^{-1}; ^1H NMR (500 MHz) δ = 1.05 (3H, d, J = 6.1 Hz), 2.00 (3H, s), 2.08 (3H, s), 3.59 (1H, dd, J = 9.7, 6.1 Hz), 4.06 (1H, dd, J = 11.0, 9.1 Hz), 4.71 (1H, t, J = 9.5 Hz), 5.24 (1H, dd, J = 11.1, 9.0 Hz), 5.57 (1H, dd, J = 8.9, 8.0 Hz), 7.43−7.57 (6H, m), 7.82−7.87 (4H, m); ^{13}C NMR (125 MHz) δ = 16.91 (p), 20.61 (p), 20.73 (p), 28.33 (t, J_{C-P} = 8 Hz), 70.80 (t), 73.68 (t), 75.20 (t), 96.96 (t, J_{C-P} = 6 Hz), 128.18 (t, J_{C-P} = 15 Hz), 128.41 (t, J_{C-P} = 14 Hz), 130.55 (q, J_{C-P} = 140 Hz), 131.42 (q, J_{C-P} = 122 Hz), 131.77 (t, J_{C-P} = 11 Hz), 131.96 (t, J_{C-P} = 11 Hz), 132.35 (t, J_{C-P} = 3 Hz), 132.54 (t, J_{C-P} = 3 Hz), 169.51 (q), 169.74 (q); MS (FAB) Found: $(M + H)^+$ = 559. Anal. Found: C, 47.43; H, 4.24%. Calcd for $C_{22}H_{24}IO_7P$: C, 47.33; H, 4.33%.

(3,4-Di-*O*-acetyl-2,6-dideoxy-2-iodo-*β*-L-mannopyranosyl) diphenylphosphinate (9C-*β*): foam; IR (KBr) 3060, 2990, 1750, 1370, 1240, 730 cm^{-1}; ^1H NMR (500 MHz) δ = 1.01 (3H, d, J = 6.1 Hz), 2.05 (3H, s), 2.10 (3H, s), 4.01 (1H, dd, J = 9.9, 6.1 Hz), 4.68−4.71 (2H, m), 5.18 (1H, t, J = 9.5 Hz), 6.08 (1H, d, J = 7.4 Hz), 7.47−7.60 (6H, m), 7.79−7.84 (4H, m); ^{13}C NMR (125 MHz) δ = 17.06 (p), 20.65 (p), 20.88 (p), 29.65 (t, J_{C-P} = 6 Hz), 68.40 (t), 68.98 (t), 72.04 (t), 96.70 (t, J_{C-P} = 6 Hz), 128.55 (t, J_{C-P} = 13 Hz), 128.75 (t, J_{C-P} = 14 Hz), 130.29 (q, J_{C-P} = 139 Hz), 130.75 (q, J_{C-P} = 136 Hz), 131.33 (t, J_{C-P} = 11 Hz), 131.64 (t, J_{C-P} = 10 Hz), 132.56 (t, J_{C-P} = 2 Hz), 132.69 (t, J_{C-P} = 4 Hz), 169.51 (q), 169.87 (q); HRMS (FAB) found: $(M + H)^+$ = 559.0323, calcd for $C_{22}H_{25}IO_7P$: M + H = 559.0383.

Reduction of Iodide with Triethylborane System. To a solution of (3,4,6-tri-*O*-acetyl-2-deoxy-2-iodo-α-D-mannopyranosyl) diphenylphosphinate (**9A-**α) (209.4 mg, 0.34 mmol) in 1,4-cyclohexadiene (2.4 mL) was added triethylborane (1 M, THP, 4.0 mL), the mixture was stirred for 2 h at 0 °C under aerobic conditions, and then triethylborane (1 M, THP, 4.0 mL) was added again and stirred for 2 h. After removal of the solvent under reduced pressure, the residue was purified by preparative TLC on silica gel using hexane:ethyl acetate (1:2) as an eluent. (3,4,6-Tri-*O*-acetyl-2-deoxy-α-D-mannopyranosyl) diphenylphosphinate (**11A-**α) was obtained in 88% yield (146.6 mg).

(3,4,6-Tri-*O*-acetyl-2-deoxy-α-D-mannopyranosyl) diphenylphosphinate (**11A-**α); foam; IR (neat) 3060, 2960, 1750, 1240, 1050 cm^{-1}; ^1H NMR (500 MHz) δ = 1.94−2.04 (10H, m), 2.44 (1H, ddd, J = 13.5, 5.2, 1.3 Hz), 3.65 (1H, dd, J = 12.5, 2.2 Hz), 4.05 (1H, ddd, J = 9.9, 3.7, 2.2 Hz), 4.19 (1H, dd, J = 12.6, 3.7 Hz), 5.06 (1H, t, J = 9.9 Hz), 5.45 (1H, ddd, J = 11.6, 9.8, 5.2 Hz), 6.02 (1H, dd, 7.3, 2.4 Hz), 7.45−7.59 (6H, m), 7.78−7.84 (4H, m); ^{13}C NMR (125 MHz) δ = 20.57 (p), 20.61 (p), 20.84 (p), 35.81 (s, J_{C-P} = 6 Hz), 61.38 (s), 68.24 (t), 68.57 (t), 69.74 (t), 93.50 (t, J_{C-P} = 5 Hz, 1-C), 128.51 (t, J_{C-P} = 13 Hz), 128.66 (t, J_{C-P} = 14 Hz), 130.64 (q, J_{C-P} = 138 Hz), 131.26 (q, J_{C-P} = 135 Hz), 131.37 (t, J_{C-P} = 10 Hz), 131.61 (t, J_{C-P} = 10 Hz), 132.51 (t, J_{C-P} = 3 Hz), 132.54 (t, J_{C-P} = 3 Hz), 169.60 (q), 170.16 (q), 170.53 (q); HRMS (FAB) found: $(M + H)^+$ = 491.1450, calcd for $C_{24}H_{28}O_2P$: M + H = 491.1471.

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Supporting Information Available: Copies of ^{1}H NMR spectra for all compounds described in the article. This material is available free of charge via the Internet at http://pubs.acs.org.

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