curio ketone **8c** as predominantly one diastereomer.[15] Oxymercuration of (*E*)-**5c** gave, as expected, predominantly the diastereomeric α-mercurio ketone epi-**8c**; in both cases, the diastereoselectivity of the oxymercuration reaction approaches 90%. The absolute configuration at C_6 of these intermediates remains to be established. Under normal Ferrier reaction conditions, (*Z*)-**5c** and (*E*)-**5c** afford the same ratio of inosose diastereomers, indicating that the configuration at the mercury-bearing carbon of **8c** has no influence on the stereochemical outcome of the aldol reaction.

Although **8c** appears to be remarkably stable as a dilute solution in aprotic solvents, exposure to Lewis acids results in rapid conversion to the inososes **7c**, **12c**, **13c**, and **14c**. Exploratory experiments indicate that the product ratio is highly dependent upon the Lewis acid promoter (Table II). Interestingly, the $SnCl_4$-promoted cyclization of **8c** is significantly more stereoselective than the cyclization of epi-**8c**. Clearly, the Lewis acid promoted version of the Ferrier reaction offers new possibilities for stereochemical control in intramolecular aldol reactions, and further characterization of this process is underway. In addition, application of this methodology to the total synthesis of biologically interesting inositol polyphosphates is in progress and will be reported in subsequent publications.[16]

Acknowledgment. This research was supported by University of California Cancer Research Coordinating Committee funds (Grant CRCC 12894).

Supplementary Material Available: Experimental details and characterization data for new compounds **5a–d**, **7a–d**, **8c**, **9c,d**, **10a–d**, **11b,c**, **12a–d**, **13c**, and **14c** (12 pages). Ordering information is given on any current masthead page.

(15) In some experiments, an initial oxymercuration adduct **15** (corresponding to the first intermediate in Scheme II) was obtained as the initial product, which, upon standing, lost MeOH at a variable rate to give **8c**.

(16) One application of this methodology may be found in the accompanying paper: Estevez, V. A.; Prestwich, G. D. *J. Am. Chem. Soc.*, following paper in this issue.

Synthesis of Enantiomerically Pure, P-1-Tethered Inositol Tetrakis(phosphate) Affinity Labels via a Ferrier Rearrangement

Virginia A. Estevez and Glenn D. Prestwich*

Department of Chemistry, State University of New York Stony Brook, New York 11794-3400

Received September 3, 1991

D-*myo*-Inositol 1,4,5-tris(phosphate) (IP_3) (**1**) (Figure 1) is an intracellular second messenger that mediates the release of calcium from nonmitochondrial stores[1] via binding to a transmembrane receptor protein.[2] Several other inositol polyphosphates have also been implicated in the regulation of calcium levels.[3] Of these, D-*myo*-inositol 1,3,4,5-tetrakis(phosphate) (IP_4) (**2**) may control regulation of Ca^{2+} reentry into the cell and modulate the IP_3-sensitive Ca^{2+} pools.[3c] Clarification of the physiological role of IP_4 would be facilitated by the isolation and characterization of its cellular receptor (IP_4R). Recently, we reported the synthesis[4]

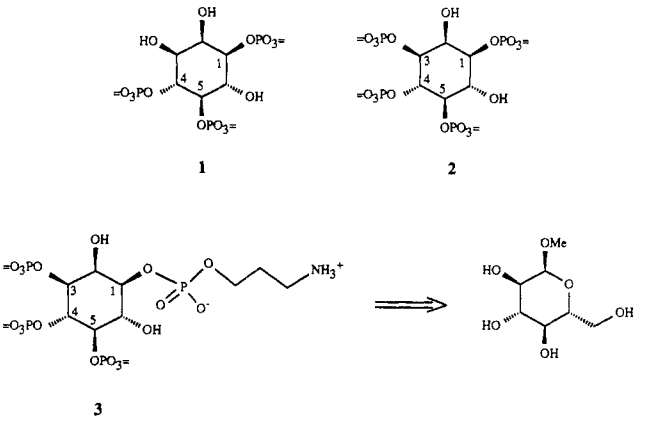
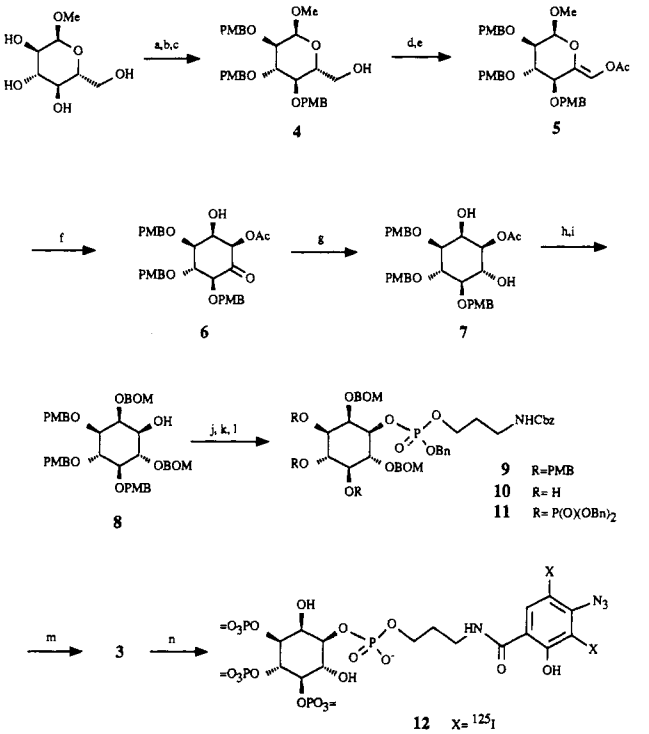


Figure 1. D-*myo*-Inositol 1,4,5-tris(phosphate) (IP_3, **1**), D-*myo*-inositol 1,3,4,5-tetrakis(phosphate) (IP_4, **2**), and derivation of P-1-modified IP_4 from the glucose carbon skeleton.

Scheme I[a]



[a] Reagents and conditions: (a) Trityl chloride, DAP, Et_3N, DMF, room temperature, 12 h; (b) NaH, PMB-Cl, DMF, reflux, 12 h; (c) 5% H_2SO_4–MeOH, acetone, room temperature, 30 min; (d) oxalyl chloride, DMSO, Et_3N, CH_2Cl_2, −78 °C to room temperature; (e) Ac_2O, K_2CO_3, CH_3CN, 80 °C, 8 h; (f) (i) $Hg(OAc)_2$, 3:2 acetone: water, room temperature, 30 min; (ii) saturated NaCl, room temperature, 24 h; (g) $NaBH(OAc)_3$, HOAc, CH_3CN, room temperature, 30 min; (h) BOM-Cl, Bu_4NBr, H^+ sponge, CH_3CN, room temperature, to 35 °C, to 55 °C; (i) NaOH, MeOH, reflux, 2 h; (j) (i) (*i*-Pr_2N)(OBn)P($OCH_2CH_2CH_2NHCbz$), tetrazole, CH_2Cl_2, room temperature, 3 h; (ii) MCPBA, −48 °C for 3 min, 0 °C for 15 min; (k) DDQ, wet CH_2Cl_2, room temperature, 6 h; (l) (i) $(BnO)_2P$(*i*-Pr_2N), tetrazole, CH_2Cl_2, room temperature, 12 h; (ii) MCPBA, −48 °C to room temperature, 2 h; (m) (i) Pd–C, H_2, 95% EtOH, 50 psi, room temperature, 5.5 h; (ii) Na-Chelex chromatography; (n) (i) NHS–ASA, DMF, 0.25 M TEAB (pH 8.0), room temperature, 12 h; (ii) DEAE cellulose chromatography; (iii) [^{125}]NaI, Iodobeads, 100 mM Na_2HPO_4 (pH 7.5), room temperature, 10 min.

of a P-1-tethered[5] derivative of racemic IP_4 (**3**) and the corresponding bioaffinity matrix which allowed isolation and purifi-

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cation of rat brain IP_4R.[6] The application of a radioiodinated photoaffinity analogue, [^{125}I]ASA-IP_4, for identification of specific binding subunits has also been described (ASA = 4-azidosalicylamide).[7] However, since the receptor only recognizes the D isomer of IP_4,[8] we now describe a novel route to enantiomerically pure,[9] P-1-tethered IP_4 via a Ferrier rearrangement[10] of a suitably protected D-glucose derivative.

Selective modification required a protecting-group strategy that would differentiate the C-1 hydroxyl from the other three hydroxyls destined for phosphorylation. The stereochemical requirements of *myo*-inositol and the disposition of the phosphates in IP_4 can be readily satisfied by a Ferrier rearrangement of a selectively protected D-glucose derivative[11] (Figure 1). The synthesis of the optically active C-1 phosphodiester analogue of IP_4 bearing a reactive aminopropyl tether is summarized in Scheme I. Tritylation of methyl α-D-glucopyranoside[12] followed by treatment with NaH and *p*-methoxybenzyl chloride provided the fully protected pyranoside in 63% overall yield. Selective detritylation was achieved in 90% yield with 5% H_2SO_4–MeOH and acetone as a cosolvent.[13] Swern oxidation of alcohol **4** provided the aldehyde (>90% hydrated), and treatment with Ac_2O and K_2CO_3 gave the (*Z*)-enol acetate **5** in 85% yield from **4**.[14] Ferrier rearrangement of **5** in the presence of mercuric trifluoroacetate and aqueous NaCl furnished the inosose **6** with the desired axial stereochemistry at the 2-OH (less than 10% equatorial)[10] in 60% yield. Stereoselective reduction of the β-hydroxy ketone with sodium triacetoxyborohydride[15] provided the *myo*-inositol skeleton **7** with the C-1 position differentially protected from the C-3, C-4, and C-5 hydroxyls.

We then focused on protecting the two remaining hydroxyls in diol **7**. For racemic, P-1-tethered IP_4,[4] hydrogen-labile benzyl protecting groups were employed at the C-2 and C-6 hydroxyls. Since base lability and ease of migration of the acetyl group can cause serious problems in polyhydroxy derivatives, benzylation at the C-2 and C-6 hydroxyls required mild, neutral conditions. Benzylation using the trichloroacetimidate method was unsuccessful due to the low solubility of the diol **7** and the acid sensitivity of the *p*-methoxybenzyl (PMB) groups. Instead, the more reactive benzyloxymethyl (BOM) group was selected. Although reaction of diol **7** with benzyloxymethyl chloride and diisopropylethylamine[16] failed, the BOM groups were readily introduced at C-2 and C-6 in 69% yield with BOM-Cl, H^+ sponge, and n-Bu_4NBr in CH_3CN.[17] To minimize acetyl migration, the BOM groups were introduced stepwise (23 °C for 10 h, 35 °C for 8 h, then 55 °C for 3 h). Basic methanolysis gave the C-1 alcohol **8** (95%), which served as the pivotal intermediate to a series of enantiomerically pure, P-1-modified IP_4 analogues.

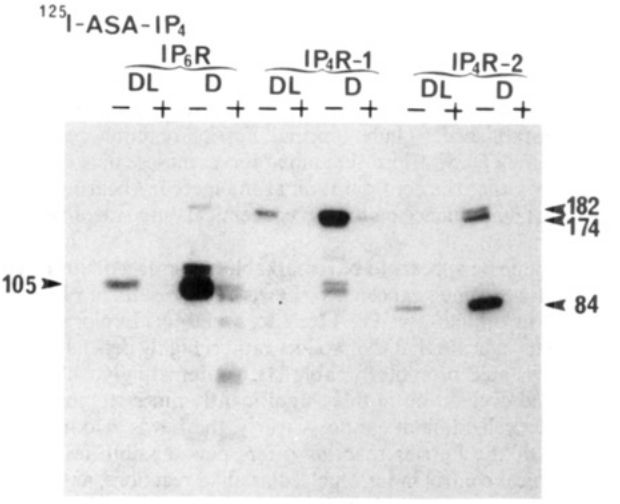

Figure 2. Photoaffinity labeling of purified IP_4 and IP_6 receptors by racemic (DL) and optically active (D) IP_4 photolabel **13**. Proteins purified from rat cerebellum by IP_4 affinity chromatography[6] were photolabeled with **13** (10 nM) as described in the absence (−) or presence (+) of 200 μM IP_4.[7] DL and D preparations of **13** were nominally of the same specific activity, based on synthesis using identical amounts and aliquots of the same batch of [^{125}]NaI; equal molar equivalents were present in each incubation sample. IP_6R is the first eluting peak, and IP_4R-1 and IP_4R-2 are the second and third eluting peaks from the affinity column;[6] the molecular sizes (in kDa) of the major bands are indicated.

Condensation of the alcohol **8** with (benzyloxy)[(3-(*N*-carbobenzoxyamino)propyl)oxy](diisopropylamino)phosphine[5c] in the presence of tetrazole and subsequent oxidation with MCPBA furnished the fully protected aminopropyl-tethered inositol **9** in 85% yield. Removal of the PMB groups with DDQ in wet CH_2Cl_2 gave the triol **10** in 78% yield after SiO_2 chromatography. Phosphitylation of the triol followed by MCPBA oxidation (as for **8**) gave the fully protected IP_4 derivative **11** (73% yield). Hydrogenolysis removed the benzyl and BOM groups to provide the optically active, P-1 aminopropyl tethered D-*myo*-Ins(1,3,4,5)P_4 (**3**) in quantitative yield after ion-exchange chromatography (Chelex, sodium form). The proton-decoupled ^{31}P NMR spectrum of this compound showed four singlets, δ 0.48, 3.59, 4.21, and 5.29 ppm, corresponding to the C-1 phosphodiester and the C-3, C-4, and C-5 phosphates, respectively.

Coupling **3** to *N*-hydroxysuccinimide-activated agarose (Affi-Gel 10) buffered at pH 8.5 provided an enantiomerically pure IP_4 affinity column, which has been employed in the purification of the IP_4R (data not shown).[18] Furthermore, reaction of this intermediate with *N*-hydroxysuccinimide 4-azidosalicylate in aqueous DMF, followed by radioiodination using Iodobeads, furnished the enantiomerically pure D-[^{125}I]ASA-IP_4 photolabel **12**. Figure 2 compares the efficacy of the optically active photolabel with that of the racemic material. It is evident from the intensity of the bands that D-**12** is a substantially more sensitive and efficient probe than DL-**12** for active-site modification of the IP_n binding sites of these receptors.

Optically active derivatives of IP_4 modified at C-1 are now readily produced via a Ferrier rearrangement of glucose. Applications of this methodology in the synthesis of C-1 tritium labeled D-IP_4 and its photolabile derivatives for the characterization of the IP_4 binding site are in progress.

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(12) Chaudhary, S. K.; Hernandez, O. *Tetrahedron Lett.* **1979**, 95–98.

(13) (a) Conventional detritylation with trifluoroacetic acid/CH_2Cl_2 resulted in partial removal of the *p*-methoxybenzyl groups. (b) All compounds were fully characterized by ^{1}H, ^{13}C, and ^{31}P NMR, FAB-MS, and for new compounds, elemental analysis.

(14) Cook, S. L.; Secrist, J. A., III. *J. Am. Chem. Soc.* **1979**, *101*, 1554–1564.

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Supplementary Material Available: Full experimental and spectral details for this synthesis (10 pages). Ordering information is given on any current masthead page.

Catalytic Asymmetric Synthesis of Optically Active 2-Alkanols via Hydrosilylation of 1-Alkenes with a Chiral Monophosphine–Palladium Catalyst

Yasuhiro Uozumi and Tamio Hayashi*

Catalysis Research Center and Graduate School of Pharmaceutical Sciences Hokkaido University, Kita-ku, Sapporo 060, Japan

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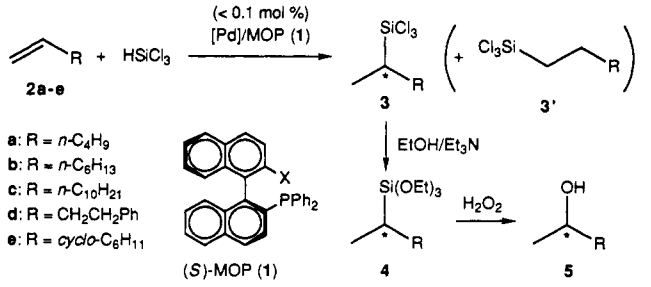
Catalytic asymmetric functionalization of simple prochiral olefins is an important goal in synthetic organic chemistry.[1,2] We report here the first successful conversion of alkyl-substituted terminal olefins into optically active secondary alcohols (>94% ee),[3] which is realized by palladium-catalyzed asymmetric hydrosilylation in the presence of a new chiral monodentate phosphine ligand (MOP, **1**) followed by oxidation of the carbon–silicon bond[4] (Scheme I).

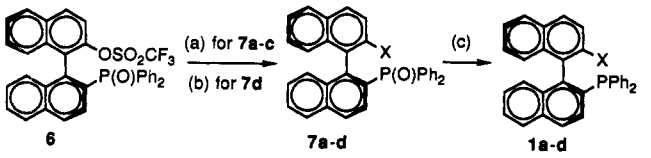
It is well-documented[5] that the hydrosilylation of terminal olefins is catalyzed by platinum, rhodium, or nickel complexes to proceed with anti-Markovnikoff selectivity leading to 1-silylalkanes. Rather surprisingly, only a little attention has been paid to the use of palladium catalysts for the hydrosilylation of 1-alkenes[6,7] in spite of their frequent use for the reaction of 1,3-dienes and styrenes.[5,6] In order to develop a catalyst possessed of high catalytic activity, high regioselectivity giving 2-silylalkanes, and high enantioselectivity in addition, we examined several types of phosphine–palladium catalysts for the reaction of 1-hexene (**2a**) with trichlorosilane. It was found that palladium complexes coordinated with a chelating bis(phosphine), dppb,[8] chiraphos,[9] or BINAP,[10] did not catalyze the hydrosilylation at 80 °C, while the reaction took place at 40 °C with monodentate phosphine ligands.[11,12] Among the monodentate phosphine ligands, (*S*)-2-(diphenylphosphino)-2′-methoxy-1,1′-binaphthyl (MOP, **1a**)[13] turned out to be by far the best ligand, giving a high yield of 2-(trichlorosilyl)hexane (**3a**) with high regioselectivity[14] as well as high enantioselectivity.

Chiral monophosphines (MOPs, **1**) are the ligands we have designed with a view to using them for the catalytic asymmetric reactions where a monophosphine ligand is required to generate a catalytically active species.[15] The present palladium-catalyzed hydrosilylation is one of the cases. The phosphines **1a–d** were readily prepared in high yields starting with known optically active

Scheme I



Scheme II[a]



(**a**: X = OMe, **b**: X = OPr-*i*, **c**: X = OCH_2Ph, **d**: X = Et)

[a] (a) (i) 3 N NaOH, 1,4-dioxane, methanol; (ii) MeI, *i*-PrI or $PhCH_2Br$ (3–10 equiv), K_2CO_3 (2–4 molar equiv), acetone, reflux, 3–24 h (**7a**, 99%; **7b**, 92%; **7c**, 87%). (b) EtMgBr (1.1 equiv), $NiCl_2$(dppe) (2 mol %), Et_2O, reflux, 24 h (**7d**, 81%). (c) Et_3N (7–20 equiv), Cl_3SiH (5 equiv), xylene, 120 °C, 3–5 h (**1a**, 97%; **1b**, 84%; **1c**, 96%; **1d**, 79%).

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(11) For example, the reaction in the presence of 0.1 mol % of a palladium–triphenylphosphine catalyst (P/Pd = 2/1) at 40 °C for 24 h gave a 12% yield of hexylsilanes consisting of 1- and 2-isomers in a ratio of 91/9, accompanied by isomerization of 1-hexene into internal olefins. See also ref 6.

(12) It is reasonable to expect that a monodentate phosphine ligand generates a palladium catalyst that is more active for the hydrosilylation than a chelating bis(phosphine) ligand. The former can form square-planar palladium(II) intermediate $PdH(SiCl_3)L(CH_2{=}CHR)$ (L = monophosphine), which offers a coordination site for the activation of olefin.

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(14) The high catalytic activity and regioselectivity of the palladium–MOP complex may be related to the reactivity of key intermediate Pd(2-alkyl)L(silyl). It seems that MOP ligand can accelerate the reductive elimination of 2-silylalkane and/or retard the β-hydrogen elimination forming 2-alkenes. Triphenylphosphine or tri-*o*-tolylphosphine caused the isomerization of a terminal olefin into internal olefins during the hydrosilylation while MOP did not (see footnote 11).

(15) An example for those reactions is nickel-catalyzed asymmetric cross-coupling: Hayashi, T.; Hayashizaki, K.; Kiyoi, T.; Ito, Y. *J. Am. Chem. Soc.* **1988**, *110*, 8153.

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