process, head-to-tail dimerization of CO_2, has often been invoked in the disproportion of CO_2. Oxygen atom transfer to CO from CO_2,[11] NO,[33] NO_2,[34] and O_2[35] has been reported. The present system is the first to display facile oxygen atom transfer from carbonate. Our studies of oxygen atom transfer from **3** to other substrates are continuing.

Acknowledgment. This work was supported by the NSF (Grant CHE-8707963). We are also grateful to the NSF for support of the Chemical X-ray Diffraction Facility at Purdue. A loan of $IrCl_3$ from Johnson-Matthey, Inc., is gratefully acknowledged.

Supplementary Material Available: Tables consisting of crystal data and data collection parameters (Table 1), positional parameters (Table 2), temperature factor expressions (Table 3), bond distances (Table 4), and bond angles (Table 5) for **3** (10 pages); a table of observed and calculated structure factors for **3** (14 pages). Ordering information is given on any current masthead page.

(40) Sharp, P. R.; Flynn, J. R. *Inorg. Chem.* **1987**, *26*, 3231.

Total Synthesis and Evaluation of (±)-*N*-(*tert*-Butyloxycarbonyl)-CBI, (±)-CBI-CDPI$_1$, and (±)-CBI-CDPI$_2$: CC-1065 Functional Agents Incorporating the Equivalent 1,2,9,9a-Tetrahydrocycloprop[1,2-*c*]benz[1,2-*e*]indol-4-one (CBI) Left-Hand Subunit

Dale L. Boger,*[1a] Takayoshi Ishizaki,[1b] Ronald J. Wysocki, Jr., and Stephen A. Munk[1c]

Department of Chemistry, Purdue University West Lafayette, Indiana 47907

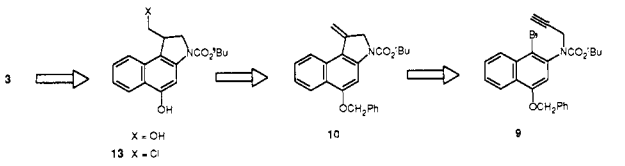
Paul A. Kitos and Oranart Suntornwat

Department of Biochemistry, University of Kansas Lawrence, Kansas 66045-2500

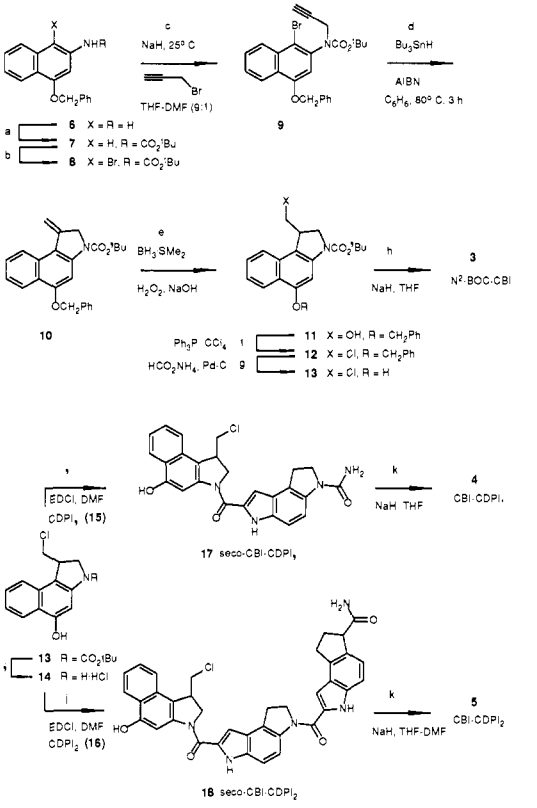
Received March 30, 1989

(+)-CC-1065 (**1**, NSC-298223), an antitumor antibiotic isolated from cultures of *Streptomyces zelensis*, possesses exceptionally potent in vitro cytotoxic activity, broad spectrum antimicrobial activity, and confirmed in vivo antitumor activity.[2-3] In a series of extensive investigations the site and mechanism of the (+)-CC-1065 antitumor activity have been related to its irreversible covalent alkylation of sequence-selective B-DNA minor groove sites [5′-d(A/GNTTA)-3′ and 5′-d(AAAAA)-3′] that has been demonstrated to proceed by 3′-adenine *N*-3 alkylation of the electrophilic cyclopropane present in the left-hand (CPI) subunit of (+)-CC-1065.[4,5] The demonstration that simplified agents including CDPI$_3$[6] methyl ester exhibit a substantial preference for A–T rich noncovalent minor groove binding[7] attributable to preferential stabilization of a noncovalent complex within the narrower, sterically more accessible A–T rich minor groove[8] (*accessible hydrophobic binding*) has suggested that CC-1065 is best represented as a selective[9] alkylating agent superimposed on the CDPI$_3$ skeleton and derives its properties in part from the effective delivery of a selective alkylating agent to accessible adenine N-3 alkylation sites. The additional demonstration that agents possessing the exceptionally reactive, parent 1,2,7,7a-tetrahydrocycloprop[1,2-*c*]indol-4-one (CI) left-hand subunit, e.g., CI-CDPI$_x$ (x = 1, 2),[10] or the unnatural enantiomer of the CC-1065 left-hand subunit (CPI), e.g., (-)-CPI-CDPI$_2$[11,12] and

Scheme I



Scheme II[a]



[a] (a) 2.0 equiv of $(tBuO_2C)_2O$, dioxane, 95 °C, 3 h, 96%; (b) 1.2 equiv of *N*-bromosuccinimide, catalytic H_2SO_4, THF, -60 °C, 5 h, 98%; (c) 1.3 equiv of NaH, 3.0 equiv of 3-bromopropyne, 24 °C, 3 h, 100%; (d) 2.0 equiv of Bu_3SnH, 0.2 equiv of AIBN, benzene, 80 °C, 1 h; (e) 6.3 equiv of $Me_2S{\cdot}BH_3$, THF, 0–25 °C, 3 h; 2 N NaOH, 30% H_2O_2, 0–25 °C, 1 h, 45 °C, 20 min, 62% from **9**; (f) 2.0 equiv of Ph_3P, 6 equiv of CCl_4, CH_2Cl_2, 24 °C, 10 h, 99%; (g) 25% aqueous HCO_2NH_4/THF 1:5, 10% Pd/C, 0 °C, 2.5 h, 97%; (h) 3 equiv of NaH, THF, 24 °C, 2 h, 93%; (i) 3 N anhydrous HCl/EtOAc, 24 °C, 10 min, 100%; (j) for **17**, 3 equiv of EDCI, 1.0 equiv of **15**, 5 equiv of $NaHCO_3$, DMF, 24 °C, 3 h, 86%; for **18**, 3 equiv of EDCI, 1.0 equiv of **16**, DMF, 24 °C, 5 h, 78%; (k) for **4**, 5 equiv of NaH, THF, 24 °C, 2 h, 74%; for **5**, 2 equiv of NaH, 2:1 THF–DMF, 0 °C, 1 h, 84%.

(1) (a) National Institutes of Health career development award recipient, 1983–1988 (CA 01134), Alfred P. Sloan fellow, 1985–1989. (b) On leave from Kyorin Pharmaceutical Co., Ltd., Tochigi, Japan. (c) American Cancer Society postdoctoral fellow (ACS no. PF-3311).

(2) Reynolds, V. L.; McGovren, J. P.; Hurley, L. H. *J. Antibiot.* **1986**, *39*, 319. Hurley, L. H.; Needham-VanDevanter, D. R. *Acc. Chem. Res.* **1986**, *19*, 230.

(3) Boger, D. L.; Coleman, R. S. *Studies in Natural Products Chemistry*; Atta-ur-Rahman, Ed.; Elsevier: Amsterdam, 1989; Vol. 3.

(4) Wierenga, W.; Bhuyan, B. K.; Kelly, R. C.; Krueger, W. C.; Li, L. H.; McGovren, J. P.; Swenson, D. H.; Warpehoski, M. A. *Adv. Enzyme Regul.* **1986**, *25*, 141.

(5) Warpehoski, M. A.; Gebhard, I.; Kelly, R. C.; Krueger, W. C.; Li, L. H.; McGovren, J. P.; Prairie, M. D.; Wicnienski, N.; Wierenga, W. *J. Med. Chem.* **1988**, *31*, 590.

(6) Boger, D. L.; Coleman, R. S.; Invergo, B. J. *J. Org. Chem.* **1987**, *52*, 1521.

(7) Boger, D. L.; Coleman, R. S.; Invergo, B. J.; Zarrinmayeh, H.; Kitos, P. A.; Thompson, S. C.; Leong, T.; McLaughlin, L. W. *Chem. Biol. Interact.*, in press. CDPI$_3$ methyl ester has been shown to exhibit a 2.6–2.2 kcal preference for minor groove binding to poly[dA]·poly[dT] and poly[d(A-T)]·poly[d(A-T)] versus poly[dG]·poly[dC].

(8) Nelson, H. C. M.; Finch, J. T.; Luisi, B. F.; Klug, A. *Nature (London)* **1987**, *330*, 221. Coll, M.; Frederick, C. A.; Wang, A. H.-J.; Rich, A. *Proc. Natl. Acad. Sci. U.S.A.* **1987**, *84*, 8385. Coll, M.; Aymami, J.; van der Marel, G. A.; van Boom, J. H.; Rich, A.; Wang, A. H.-J. *Biochemistry* **1989**, *28*, 310.

(9) Hurley, L. H.; Lee, C.-S.; McGovren, J. P.; Warpehoski, M. A.; Mitchell, M. A.; Kelly, R. C.; Aristoff, P. A. *Biochemistry* **1988**, *27*, 3886.

(10) Boger, D. L.; Wysocki, R. J., Jr. *J. Org. Chem.* **1989**, *54*, 1238.

(11) Boger, D. L.; Coleman, R. S. *J. Am. Chem. Soc.* **1988**, *110*, 4796.

(12) Boger, D. L.; Munk, S. A.; Bina, M., unpublished observations, Supplementary Material.

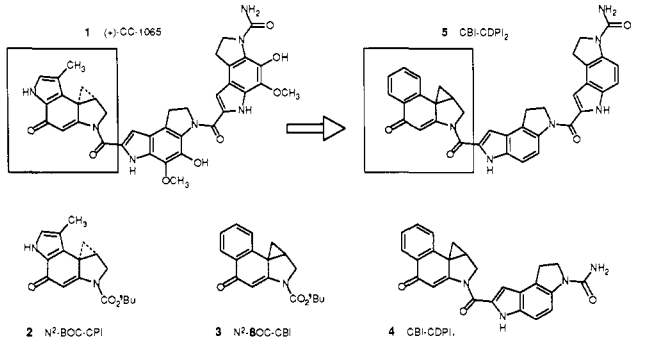
0002-7863/89/1511-6461$01.50/0

Table I

	(+)-CC-1065 **1**	(±)-BOC-CPI **2**	(±)-BOC-CBI **3**	(±)-CBI-CDPI$_1$ **4**	(±)-CBI-CDPI$_2$ **5**	(±)-CBI
$t_{1/2}$,[b] pH = 3.0		35.5 h (38.5 h)[a]	132 h			stable
$t_{1/2}$, pH = 7.0	stable	stable	stable	stable	stable	stable
$t_{1/2}$ (rel)		1.0	3.7			>10–20
IC_{50},[c] (10^{-5} μg/mL)						
L1210	1.2 (1.5)	10000	1500 (4700)	0.2 (0.9)	1.3 (1.4)	190
B16	1.4 (11)	>100000	38000 (13000)	5.0 (7)	1.6 (5)	530

[a] Taken from ref 5. [b] Half-life ($t_{1/2}$) in 50% H_2O–CH_3OH at pH = 7, and 50% CH_3OH–buffer at pH = 3 as monitored by UV. Buffer is 4:1:20 (v/v) 0.1 M citric acid, 0.2 M Na_2HPO_4, and water. [c] IC_{50} = inhibitory concentration for 50% cell growth of L1210 mouse lymphocytic leukemia and mouse B16 melanoma relative to untreated controls, see ref 23. The value in parentheses refers to the chloromethyl seco agents, e.g., **13**, **17**, and **18**.

(−)-CC-1065,[11-13] exhibit the CPI-characteristic sequence-selective covalent alkylation of DNA has suggested that the specificity of the adenine N-3 alkylation is a function of DNA structure[14] and may *not* be uniquely embodied in the natural left-hand subunit of CC-1065.[9] Further, the thermal neutral nature of the adenine-CPI DNA alkylation (estimated $\Delta H°$ = 1.5 to −3.9 kcal)[16-18] has suggested that it is the dominant noncovalent binding of the agents that drives the thermodynamically poor covalent alkylation (*binding-driven-bonding*). In support of this, the substantially reduced DNA binding efficiency and cytotoxic properties of CPI (ca. 10000*x*) versus the comparable or indistinguishable properties of the aborted functional analogues of (+)-CC-1065, e.g., (+)-CPI-CDPI$_1$ and (+)-CPI-PDE-I$_1$,[15] have confirmed that an important and additional functional role of the (+)-CC-1065 central subunit is to promote and stabilize the DNA:CC-1065 covalent complex formation (*binding-driven-bonding*). Herein we detail the total synthesis and preliminary evaluation of (±)-*N*-(*tert*-butyloxycarbonyl)-CBI (**3**), (±)-CBI-CDPI$_1$ (**4**), and (±)-CBI-CDPI$_2$ (**5**) constituting functional analogues of CC-1065 incorporating the *equivalent* 1,2,9,9a-tetrahydrocycloprop[1,2-*c*]-benz[1,2-*e*]indol-4-one (CBI) left-hand subunit. In anticipation that structural variations (e.g., CPI → CBI) of the left-hand subunit of the agents would not preclude a relevant adenine N-3 alkylation,[10] the comparable heats of reaction ($\Delta H°$)[16-18] for CPI-adenine and CBI-adenine covalent alkylation suggested that the fundamental features of the DNA covalent alkylation characteristics of (+)-CC-1065 and the CPI-based agents (accessible hydrophobic binding-driven-bonding) would be embodied in the more accessible CBI-based agents *in an equivalent manner.*



Alkylation of the sodium salt of 2-((*tert*-butyloxycarbonyl)-amino)-4-(benzyloxy)-1-bromonaphthalene (**8**)[19] with 3-bromopropyne provided **9**, the immediate precursor for implementation of a 5-exo-dig aryl radical-alkyne cyclization,[20] Scheme II. Treatment of **9** with tri-*n*-butyltin hydride under conditions previously detailed[11] provided the unstable 3-methyleneindoline **10** which was subjected immediately to the conditions of hydroboration–oxidation to provide **11**. Conversion of the primary alcohol **11** to the primary chloride **12** (Ph_3P, CCl_4),[21] two-phase transfer catalytic hydrogenolysis (HCO_2NH_4, 10% Pd/C) of the benzyl ether which proved to proceed without competitive hydrogenolysis of the primary chloride provided **13** as a stable, immediate precursor to **3–5**. Intramolecular Ar-3′ alkylation of **13** promoted by the treatment of **13** with sodium hydride (THF, 24 °C, 2.5 h) cleanly provided N^2-(*tert*-butyloxycarbonyl)-CBI (**3**, 93%). The incorporation of the CBI left-hand subunit into two functional analogues of CC-1065, CBI-CDPI$_1$ (**4**) and CBI-CDPI$_2$ (**5**), is detailed in Scheme II. Treatment of **13** with anhydrous hydrochloric acid (3 N HCl/EtOAc, 10 min, 24 °C) afforded the unstable hydrochloride **14** that was coupled directly with CDPI$_1$[6] (**15**, 3-carbamoyl-1,2-dihydro-3*H*-pyrrolo[3,2-*e*]-indole-7-carboxylic acid) and CDPI$_2$[6] (**16**) in the presence of 1-[(3-dimethylamino)propyl]-3-ethylcarbodiimide to provide **17** (86%) and **18** (78%),[22] respectively. Final Ar-3′ alkylative ring closure of **17** and **18** (NaH, 24 °C) provided CBI-CDPI$_1$ (**4**) and CBI-CDPI$_2$ (**5**).

Table I details the results of the preliminary evaluation and comparison of the properties and stability of the CBI-based versus CPI-based agents. Like CPI, the CBI-based agents proved stable in aqueous solution at pH = 7, and consistent with expectations N^2-BOC-CBI proved to be more stable than N^2-BOC-CPI to solvolysis at pH = 3, Table I. The cytotoxic potency of the CBI-based agents has proven equipotent to that observed with the potent CPI-based agents (*N*-BOC-CBI > *N*-BOC-CPI, CBI-CDPI$_2$ ≡ (+)-CC-1065), and full details of this comparison

(13) Kelly, R. C.; Gebhard, I.; Wicnienski, N.; Aristoff, P. A.; Johnson, P. D.; Martin, D. G. *J. Am. Chem. Soc.* **1987**, *109*, 6837.

(14) Hurley, L. H.; Warpehoski, M. *Chem. Res. Toxicol.* **1988**, *1*, 328. The intended[3] use of "accessible hydrophobic binding-driven-bonding" to describe the CC-1065:DNA association has been misrepresented in this recent review. Nonetheless, we thank the authors for extending the intended description to include additional DNA:agent associations. Our use of "binding-driven-bonding" did not state that binding selectivity dominates bonding selectivity. It simply productively contributes to it. Rather, it was intended to describe the relatively thermal neutral bonding reaction that is stabilized (driven) by the strong, dominant, noncovalent binding of the agent. The noncovalent stabilization in turn is derived predominantly from stabilizing van der Waals contacts and hydrophobic binding with preferential binding within the narrower, sterically more accessible A–T rich minor groove.

(15) Boger, D. L.; Coleman, R. S.; Invergo, B. J.; Sakya, S.; Munk, S.A.; Kitos, P. A.; Thompson, S. C. submitted for publication.

(16) AM1: Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902.

(17) MNDO: Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899.

(18) Errors inherent in the calculated heats of formation[16] (Supplementary Material) suggest that accurate estimates of the heats of reaction for the adenine N-3 alkylation lie in the range of +1.5 to −3.9 kcal (AM1, MNDO) and +4.4 to −1.6 kcal (AM1, MNDO) for CPI and CBI, respectively. This relatively thermal neutral adenine N-3 alkylation coupled with the additional nonbonded destabilization of double-stranded DNA that accompanies the covalent alkylation and the additional, albeit small, conformational destabilization of the agent and DNA required to permit binding places the CPI/CBI alkylation of DNA close to a destabilizing event. The experimentally verified stability of the CPI-based agents toward even simple nucleophilic additions to the activated cyclopropane attest to their modest electrophilic character.

(19) 3-Amino-1-(benzyloxy)naphthalene (**6**) was prepared from commercially available 1,3-dinitronaphthalene: (i) 2 equiv of $NaOCH_3$, CH_3OH, 105 °C, 7 h, cf. Hanker, J. S.; Katzoff, L.; Aronson, L. D.; Seligman, M. L.; Rosen, H. R.; Seligman, A. M. *J. Org. Chem.* **1965**, *30*, 1779; (ii) 1:1 48% aqueous HBr–HOAc, reflux, 6 h, 91%; (iii) 1.1 equiv of $C_6H_5CH_2Br$, 2.1 equiv of K_2CO_3, 0.03 equiv of Bu_4NI, DMF, 25 °C, 3 h, 97%; (iv) Al(Hg) prepared from 26 mol equiv of Al, 10% aqueous THF, 25 °C, 2.5 h, 99%.

(20) Curran, D. P. *Synthesis* **1988**, 417 and 489.

(21) Hooz, J.; Gilani, S. S. H. *Can. J. Chem.* **1968**, *46*, 86.

(22) The slow coupling of **14** with the insoluble CDPI$_2$ (**16**) in the presence of sodium bicarbonate (5.0 equiv) provided predominately CBI. CBI was effectively prepared by deliberate cyclization of **14** (5% aqueous $NaHCO_3$–THF (1:1), 25 °C, 1.5 h, 80%).

will be disclosed in a full account of this work. Evidence for the covalent alkylation of DNA by the CBI-based agents was obtained from the thermally-induced strand cleavage of double-stranded DNA after exposure to the agents (autofootprinting),[9] Figure 1 (Supplementary Material). The autofootprinting was carried out with a 5′-end labeled fragment of SV40 (144 bp fragment, bp 138–5238) cloned into the Sma I site of the M13mp10 polylinker region [Agent:DNA incubation at 4 °C, 24 h; removal of unreacted agent through ethanol precipitation of DNA; thermal cleavage at 100 °C, 30 min].[24] Gel electrophoresis and autoradiographic evaluation of the DNA revealed that the observed sites of covalent alkylation and their relative intensities for CBI, **4**, **5**, and (+)-CC-1065 are identical.

The identical DNA binding properties of (±)-CBI-CDPI$_2$ (**5**) and (+)-CC-1065 (**1**) and their equipotent cytotoxic activity [IC_{50} (10^{-5} μg/mL), L1210: 1.2 (**1**) and 1.3 (**5**), B16: 1.4 (**1**) and 1.6 (**5**)] establishes that CBI-CDPI$_2$ constitutes an equivalent functional analogue of (+)-CC-1065 that embodies the fundamental and precise functional features of the agent responsible for its properties. Additional studies on the CBI-based agents will be disclosed in due course.

Acknowledgment. This work was assisted through the financial support of the National Institutes of Health (D.L.B., CA 41986; P.A.K., ES 03651), the Alfred P. Sloan Foundation, and American Cyanamid. We thank Dr. B. J. Invergo for early experimental contributions to this work.

Supplementary Material Available: Full physical and spectroscopic characterization of **3–5**, **6–13**, **17**, and **18**, a table of the full comparative properties of the CBI and CPI agents (Table I), additional details of the computational studies (eq 1), descriptive experimental and a summary of a series of autofootprinting studies (Figure 1), and a figure (Figure 2) representing the binding of (+)-CBI-CDPI$_2$ within a high affinity SV40 DNA binding site (15 pages). Ordering information is given on any current masthead page.

(23) Boger, D. L.; Yasuda, M.; Mitscher, L. A.; Drake, S. D.; Kitos, P. A.; Thompson, S. C. *J. Med. Chem.* **1987**, *30*, 1918.
(24) A summary of the autofootprinting study is provided as Supplementary Material.

Samarium(II) Iodide Mediated Transformation of Carbohydrates to Carbocycles

Eric J. Enholm* and Antigone Trivellas

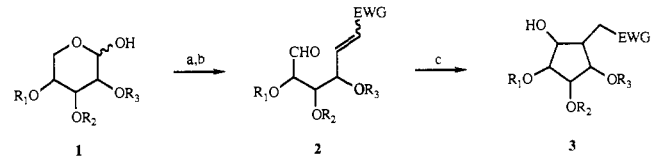
Department of Chemistry, University of Florida
Gainesville, Florida 32611

Received March 15, 1989

Recently, there has been considerable interest in the construction of carbocycles from carbohydrates with many of these reactions involving the cyclization of 5-hexenyl radicals mediated by tributyltin hydride in a key step.[1] The highly oxygenated carbocyclic products produced in this process possess considerable synthetic utility because of their application to the total synthesis of biologically important molecules such as enzyme regulators,[2a] the Corey lactone and related prostaglandin intermediates,[2b] and carbocyclic ribose derivatives.[2c,d]

A quite different solution to this synthetic problem is afforded by one-electron reducing agents and electroreductive methods which mediate a variety of carbon–carbon bond-forming processes.[3] A useful variant of this technology utilizes the reductive coupling reagent, samarium diiodide, in the intramolecular coupling of two sp^2 hybridized carbon centers in a mild and regiocontrolled ring-forming process.[4] A number of these studies involve the cyclization of aldehydes or ketones tethered to olefins which often proceed with high levels of diastereoselectivity.[5,6] We would now like to report a novel method for the stereoselective preparation of polyhydroxylated carbocycles from carbohydrate templates[7] mediated by the one-electron transfer agent, samarium diiodide. These studies also demonstrate a surprising reversal in the diastereoselectivity in the products depending on whether the olefin geometry of the starting carbohydrate is cis or trans. Finally, to our knowledge, no applications of samarium diiodide to carbohydrate templates have been studied.

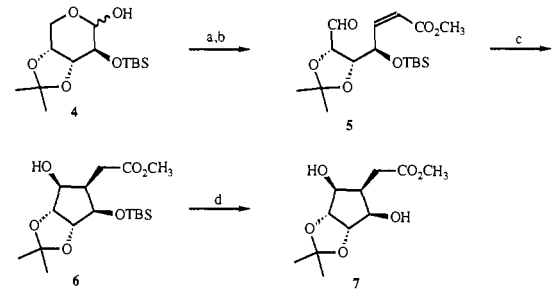
Scheme I[a]



1 2 3

[a] EWG = CO_2Me; Key: (a) $Ph_3P{=}CH{-}EWG$, H^+ (0.1 equiv), CH_2Cl_2; (b) PDC, CH_2Cl_2; (c) SmI_2, THF, MeOH, −78 °C.

Scheme II[a]



4 5 6 7

[a] Key: (a) $Ph_3P{=}CHCO_2Me$, CH_2Cl_2, $PhCO_2H$ (0.1 equiv); (b) PDC, CH_2Cl_2, 3 Å sieves, HOAc (0.1 equiv); (c) SmI_2 (2 equiv), THF, MeOH, −78 °C; (d) nBu_4NF, THF, 0 °C.

(1) (a) RajanBabu, T. V. *J. Am. Chem. Soc.* **1987**, *119*, 609. (b) Tsang, R.; Fraser-Reid, B. *J. Am. Chem. Soc.* **1986**, *108*, 2116. (c) Wilcox, C. S.; Thomasco, L. M. *J. Org. Chem.* **1985**, *50*, 546. (d) Nugent, W. A.; RajanBabu, T. V. *J. Am. Chem. Soc.* **1988**, *110*, 8561. (e) RajanBabu, T. V.; Fukunaga, T.; Reddy, G. S. *J. Am. Chem. Soc.* **1989**, *111*, 1759. (f) Vite, G. D.; Alonso, R.; Fraser-Reid, B. *J. Org. Chem.* **1989**, *54*, 2268, and references therein.
(2) (a) Wilcox, C. S.; Guadino, J. J. *J. Am. Chem. Soc.* **1986**, *108*, 3102. (b) RajanBabu, T. V. *J. Org. Chem.* **1988**, *53*, 4522. (c) Suhadolnik, R. J. *Nucleoside Antibiotics*; Wiley: New York, NY, 1970. (d) Daluge, S.; Vince, R. *J. Org. Chem.* **1978**, *43*, 2311 and references therein.
(3) For a review of these processes, see: (a) Giese, B. *Radicals in Organic Synthesis: Formation of Carbon–Carbon Bonds*; Pergamon Press: New York, NY, 1986. For recent examples, see: (b) Fox, D. P.; Little, R. D.; Baizer, M. M. *J. Org. Chem.* **1985**, *50*, 2202. (c) Little, R. D.; Fox, D. P.; Hijfte, L. V.; Dannecker, R.; Sowell, G.; Wolen, R. L.; Möens, L.; Baizer, M. M. *J. Org. Chem.* **1988**, *53*, 2287. (d) Ikeda, T.; Yue, S.; Hutchinson, C. R. *J. Org. Chem.* **1985**, *50*, 5193. (e) Corey, E. J.; Pyne, S. G. *Tetrahedron Lett.* **1983**, 2824. (f) Belotti, D.; Cossy, J.; Pete, J. P.; Portella, C. *J. Org. Chem.* **1986**, *51*, 4196. (g) Pattenden, G.; Robertson, G. M. *Tetrahedron Lett.* **1986**, 399.
(4) For reviews on lanthanide-mediated reactions, see: (a) Natale, N. R. *Org. Prep. Proced. Int.* **1983**, *15*, 387. (b) Kagan, H. B. *Fundamental and Technological Aspects of Organo-f-Element Chemistry*; Marks, T. J., Fragara, I. L., Eds.; NATO ASI: Dordrecht, 1985; pp 49–76. For recent applications of lanthanides in synthesis, see: (c) Molander, G. A.; Etter, J. B. *Tetrahedron Lett.* **1984**, 3281. (d) Molander, G. A.; Etter, J. B. *J. Org. Chem.* **1986**, *51*, 1778. (e) Molander, G. A.; Etter, J. B.; Zinke, P. W. *J. Am. Chem. Soc.* **1987**, *109*, 453. (f) Molander, G. A.; Kenny, C. *J. Org. Chem.* **1988**, *53*, 2132. (g) Molander, G. A.; Etter, J. B. *Synth. Commun.* **1987**, *17*, 901. (h) Molander, G. A.; Etter, J. B. *J. Am. Chem. Soc.* **1987**, *109*, 6556. (i) Fevig, T. L.; Elliott, R. L.; Curran, D. P. *J. Am. Chem. Soc.* **1988**, *110*, 5064 and references therein.
(5) (a) Fukuzawa, S.; Iida, M.; Nakanishi, A.; Fujinami, T.; Sakai, S. *J. Chem. Soc., Chem. Commun.* **1987**, 920. (b) Fukuzawa, S.; Nakanishi, A.; Fujinami, T.; Sakai, S. *J. Chem. Soc., Perkin Trans. I* **1988**, 1669 and references therein. (c) Molander, G. A.; Kenny, C. *Tetrahedron Lett.* **1987**, 4367.
(6) Enholm, E. J.; Trivellas, A. *Tetrahedron Lett.* **1989**, 1063.
(7) For a review of the use of carbohydrate templates in synthesis, see: Hanessian, S. *Total Synthesis of Natural Products: The "Chiron" Approach*; Pergammon Press: London, 1983.

0002-7863/89/1511-6463$01.50/0