Table I. *A* Values of Di-*p*-phenylbenzyl Ethers of Hexopyranosides, in CH_3CN

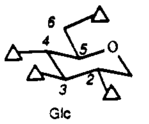
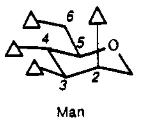
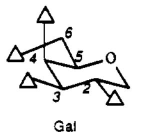
	 Glc		 Man		 Gal	
	entry	*A*	entry	*A*	entry	*A*
2,3-	**1**	+13.4 (1,2-ee)	**7**	−3.9 (1,2-ae)	**13**	+5.3 (1,2-ee)
2,4-	**2**	−5.0 (1,3-ae)	**8**	−3.6 (1,3-ae)	**14**	+6.9 (1,3-ea)
2,6-	**3**	−3.0	**9**	−3.5	**15**	0
3,4	**4**	−25.4 (1,2-ee)	**10**	−13.8 (1,2-ee)	**16**	+8.4 (1,2-ea)
3,6-	**5**	+3.9	**11**	+2.6	**17**	−2.6
4,6-	**6**	+16.1	**12**	+13.5	**18**	−13.7

Table II. Additivity in *A* Values of Tri- and Tetra-*p*-phenylbenzyl Ethers of Hexopyranosides, in CH_3CN

	glucoside			mannoside			galactoside		
	entry	obsd	calcd	entry	obsd	calcd	entry	obsd	calcd
2,3,4-	**19**	−16.4	−17.0	**24**	−21.6	−23.1	**29**	+19.4	+20.6
2,3,6-	**20**	+13.2	+14.3	**25**	−5.2	−4.8	**30**	+4.9	+2.7
2,4,6-	**21**	+9.7	+8.1	**26**	+7.2	+6.4	**31**	−8.1	−6.8
3,4,6-	**22**	−7.3	−5.4	**27**	+2.8	+2.3	**32**	−6.5	−7.9
2,3,4,6-	**23**	0	0	**28**	−9.8	−8.7	**33**	+5.1	+4.3

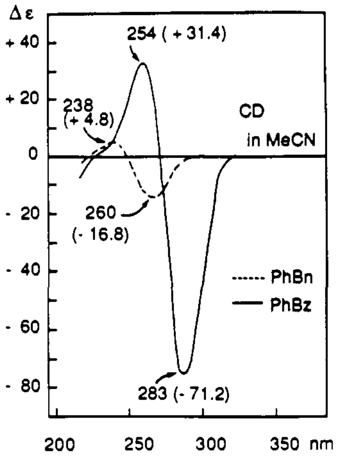


Figure 2. CD of 2,3,4-tri-*p*-phenylbenzyl ether (14.0 μg/mL or 20.2 pmol) and 2,3,4-tri-*p*-phenyl benzoate (9.0 μg/mL or 11.6 pmol) of α-methyl mannoside, in CH_3CN.

2,3,4-tribenzylate (Figure 2, *A* −21.6) vs. 2,3,4-tri-*p*-bromobenzoate (*A* −120[6]) or one-fifth sensitivity in the benzylate. However, oxidation of the ethers with ruthenium tetraoxide under conditions slightly modified from the original,[9] $RuCl_3\cdot 3H_2O/NaIO_4$ in CCl_4/CH_3CN, pH 7 aqueous buffer, 15–20 min, room temperature, converted sugar perbenzylates into corresponding benzoates in 60% yield,[10] with concomitant increase in *A* values *and* retention of additivity relation. The *A* values for following mannoside *p*-phenylbenzoates are (compare with corresponding benzylates in Table I), 2,3, −35.6, 2,4, −26.8; and 3,4, −60.5. The A_{calcd} for 2,3,4-triphenylbenzoate is −122.9, which compares well with A_{obsd} of −102.6 (Figure 2); note also 5-fold enhancement of *A* over tribenzylate.[11]

Simultaneous usage of two chromophores, the *p*-bromobenzoate (λ_{max} 244 nm) and *p*-methoxycinnamate (λ_{max} 311 nm), led to the finding that the additivity rule is valid not only for one-dimensional *A values* but more importantly for the entire *CD curve* of hexopyranoside acylates,[12] thus making *bichromophoric CD curves a characteristic of each sugar species.* In this paper we show that the *additivity rule can be extended to the more stable benzylates* and that if necessary a *ca. 5-fold enhancement in sensitivity* can be achieved by oxidation to corresponding benzoates. These findings form the basis of several micro methods under development for oligosaccharide structure studies.

Acknowledgment. We are grateful to Dr. S. Imajo for MM2 calculations. The studies were supported in part by NIH GM 34509.

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(9) Carlsen, P. H. J.; Katsuki, T.; Martin, V. S.; Sharpless, K. B. *J. Org. Chem.* **1981**, *46*, 3938.

(10) Zask, A., et al., unpublished results.

(11) A full account of this study, including all standard *A* values of pyranoside *p*-phenylbenzoates, will be submitted for publication shortly: Takeda, R.; Park, M. H.; Nakanishi, K., manuscript in preparation.

(12) Wiesler, W. T.; Vazquez, J. T.; Nakanishi, K. *J. Am. Chem. Soc.* **1986**, *108*, 6811.

Preparation of the First η^2-Olefin Complex of a 4f-Transition Metal, $(Me_5C_5)_2Yb(\mu\text{-}C_2H_4)Pt(PPh_3)_2$

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Insertion of an olefin into a metal–carbon bond is a fundamental and a reasonably well-known process in d- and f-transition metal organometallic chemistry.[1] It is generally assumed that coordination of the olefin to the metal center is a prerequisite to insertion, though no olefin complexes of an f-transition metal have been isolated, in contrast to the enormous number of olefin complexes of the d-transition metals as well as the monovalent coinage metals.[2] Recently the η^6-arene and η^2-acetylene complexes

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(1) (a) Yamamoto, A. *Organotransition Metal Chemistry*; Wiley: New York, 1986; Chapter 7. (b) Sinn, H.; Kaminsky, W. *Adv. Organomet. Chem.* **1980**, *18*, 99–149. (c) Turner, H. W.; Schrock, R. R. *J. Am. Chem. Soc.* **1982**, *104*, 2331–2333. (d) Schmidt, G. F.; Brookhart, M. *Ibid.* **1985**, *107*, 1443–1444. (e) Clawson, L.; Soto, J.; Buchwald, S. L.; Steigerwald, M. L.; Grubbs, R. H. *Ibid.* **1985**, *107*, 3377–3378. (f) Watson, P. L. *Ibid.* **1982**, *104*, 337–339. (g) Watson, P. L.; Roe, D. C. *Ibid.* **1982**, *104*, 6471–6473. (h) Watson, P. L.; Herskovitz, T. *Initiation of Polymerization*; Bailey, F. E., Ed.; ACS Symposium Series 212; American Chemical Society: Washington, DC, 1983; p 459. (i) Watson, P. L.; Parshall, G. W. *Acc. Chem. Res.* **1985**, *18*, 51–56. (j) Thomas, R. R.; Chebolm, V.; Sen, A. *J. Am. Chem. Soc.* **1986**, *108*, 4096–4103.

(2) (a) Green, M. L. H. *Organometallic Compounds*; Chapman and Hall: London, 1968; Vol. 2, Chapter 2. (b) Herberhold, M. *Metal π-Complexes*; Elsevier, Amsterdam, 1974. (c) Ittel, S. D.; Ibers, J. A. *Adv. Organomet. Chem.* **1976**, *14*, 33–61. (d) Pasquali, M.; Floriani, C.; Gaetani-Manfredotti, A.; Chiesi-Villa, A. *J. Am. Chem. Soc.* **1978**, *100*, 4918–4919. (e) Thompson, J. S.; Whitney, J. F. *Inorg. Chem.* **1984**, *23*, 2813–2819.

0002-7863/87/1509-0915$01.50/0

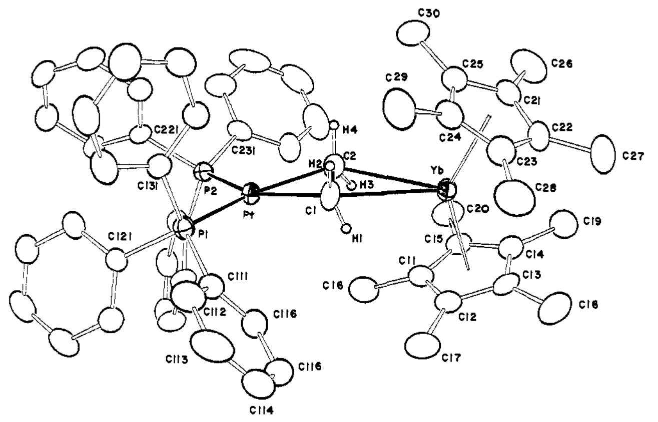

Figure 1. ORTEP diagram of I; the ellipsoids represent 50% probability surfaces, except those of the hydrogen atoms on the ethylene unit which are arbitrary.

$(Me_6C_6)Sm(AlCl_4)_3$[3a] and $(Me_5C_5)_2Yb(MeC{\equiv}CMe)$[3b] have been characterized showing that neutral π-complexes of the lanthanides can be isolated.

We have observed that the bent, base-free compound $(Me_5C_5)_2Yb$[4a] initiates the polymerization of ethylene, though not that of propylene or styrene,[4b] the mechanisms of which is unknown though it presumably involves an η^2-ethylene coordination complex. These studies encouraged us to try to isolate an olefin complex of an f-transition metal. In order to isolate such a complex, we postulated that an olefin with sterically small electron-donor groups rather than electron-withdrawing groups would maximize the Lewis basicity of the olefin donor orbitals. One way of creating such an olefin is to use a Pt(0) complex with ethylene, $(\eta^2\text{-}C_2H_4)Pt(PPh_3)_2$;[5] the olefin is electron rich since Pt(0) is a good π-donor.

Addition of white $(\eta^2\text{-}C_2H_4)Pt(PPh_3)_2$ to a toluene solution of $(Me_5C_5)_2Yb$ gives a red solution from which deep red needles of the adduct I may be isolated, mp 178–180 °C. The infrared spectrum (Nujol mull) is not greatly different from the superposition of the spectra of the individual molecules and the solution NMR spectra are consistent with a chemically exchanging system. The ${}^1H$ NMR spectrum of $(Ph_3P)_2Pt(C_2H_4)$ in C_6D_6 (30 °C, 500 MHz) shows the ethylene protons at δ 2.63 and $J(Pt\text{-}H) = 60$ Hz. The ethylene protons of I are observed (C_6D_6, 30 °C, 90 MHz) at δ 2.18 $J(Pt\text{-}P) = 56$ Hz, but the line is broadened and no other coupling information is available. At 500 MHz, 30 °C, C_6D_6, the ethylene protons are not observable, but at 50 °C a broadened singlet with satellites due to $J(Pt\text{-}H)$ begins to appear at δ 2.23 which does not appreciably sharpen to 90 °C. At −70 °C in C_7D_8 (500 MHz) the Me_5C_5 resonance is broadened and overlaps with the ethylene resonance. This behavior is characteristic of a chemical exchange process that is rapid at high temperature, intermediate at 30 °C, and apparently not stopped at −70 °C.[6]

$$(Me_5C_5)_2Yb + (\eta^2\text{-}C_2H_4)Pt(PPh_3)_2 \rightleftarrows (Me_5C_5)_2Yb(\mu\text{-}C_2H_4)Pt(PPh_3)_2$$

Although the solution spectroscopy is ambiguous relative to structure, the solid-state structure determined by X-ray diffraction at −80 °C is shown in Figure 1.[7] The $(Ph_3P)_2Pt$ and $(Me_5C_5)_2Yb$ portions of I are only slightly perturbed relative to uncomplexed $(Ph_3P)_2Pt(\eta^2\text{-}C_2H_4)$[5b] and $(Me_5C_5)_2Yb(thf)$.[8] The averaged Pt-P and Pt-C distances are 2.268 ± 0.002, 2.111 ± 0.003 Å and 2.275 ± 0.005, 2.084 ± 0.001 Å in $(Ph_3P)_2Pt(\eta^2\text{-}C_2H_4)$ and I, respectively. The P-Pt-P and C-Pt-C angles in $(Ph_3P)_2Pt(\eta^2\text{-}C_2H_4)$ and I are 111.6 (1)°, 39.7 (4)° and 106.31 (3)°, 40.3(1)°, respectively. The averaged $Yb\text{-}C(Me_5C_5)$ and $Yb\text{-}Me_5C_5$ ring centroid distances and the Me_5C_5 ring centroid-Yb-Me_5C_5 ring centroid angle in $(Me_5C_5)_2Yb(thf)$ and I are 2.66 ± 0.01 Å, 2.37 Å, 143.5° and 2.67 ± 0.02 Å, 2.39 Å, 142.3°, respectively. The Yb-C(1,2) distances in I are 2.770 (3) and 2.793 (3) Å, which average to 2.781 ± 0.006 Å, and the C(1)-Yb-C(2) angle is 29.9 (1)°. In $(Me_5C_5)_2Yb(\eta^2\text{-}MeC{\equiv}CMe)$ the equivalent parameters are 2.850 ± 0.010 Å and 23.4 (1)°.[3b] The Yb–C(olefin) distance in I is similar to the divalent Yb to semibridging methyl distance in $Yb[N(SiMe_3)_2]_2(dmpe)$[9a] of 2.77 and 2.86 Å, in $NaYb[N(SiMe_3)_2]_3$[9b] of 2.86 and 2.91 Å, and in $Yb[N(SiMe_3)_2]_2(Me_3Al)_2$[9c] which range from 2.756 (2) to 3.202 (3) Å. In addition, the Yb to olefin distance is intermediate between the long and short bridging Lu–C distance of 2.756 (9) and 2.440 (9) Å, respectively, in $(Me_5C_5)_4Lu_2(Me)(\mu\text{-}Me)$,[11] since Lu(III) is ca. 0.1 Å smaller than Yb(II) in a given coordination number.[9d]

The bridging olefin portion of I is the structural feature of principal interest. The hydrogen atoms on the olefin of I were located and refined isotropically whereas they were not located in $(Ph_3P)_2Pt(\eta^2\text{-}C_2H_4)$.[5] The averaged C-H distance is 0.96 ± 0.06 Å, the averaged H-C-H, H-C-C, and H-C-Pt angles are 117.1 ± 0.3°, 117.8 ± 2.7°, and 112.2 ± 3.5°, respectively. The C-C distance in I of 1.436 (5) Å is the same as that in $(Ph_3P)_2Pt(\eta^2\text{-}C_2H_4)$ of 1.43 (1) Å. In addition, α, the angle between the normals to the planes defined by the hydrogen atoms, is 52.7°.[2c] The intersection of the planes defined by H(1)C(1)H(2) and C(1)C(2)Pt, H(3)C(2)H(4) and C(1)C(2)Pt are 89.0° and 85.7°, respectively. Intersection of the PtC(1)C(2) and YbC(1)C(2) planes is 15.1°. This bending results in moving two of the four hydrogen atoms, H(1,3), toward the electropositive ytterbium atom, the averaged YbC(1)H(1) and YbC(2)H(3) angles being 69.5 ± 0.6° and the averaged YbC(1)H(2) and YbC(2)H(4) angles being 100.0 ± 1.4°. The bending results in two types of Yb···H contact distances, YbH(1) = 2.58 (5), YbH(3) = 2.64 (3), YbH(2) = 3.09 (4), and YbH(4) = 3.15 (3) Å. The shorter pair of distances is similar to those found in the semibridging methyl to divalent Yb distances in which two of the three hydrogens on each methyl group approach the ytterbium atom at distances of 2.53, 2.63, 2.72, and 3.13 Å in $Yb[N(SiMe_3)_2]_2(Me_3Al)_2$[9c] and the Yb···H contact distances of 2.77 and 2.86 Å in $Yb[N(SiMe_3)_2]_2(dmpe)$.[9a] The Yb···H distances are substantially longer than those found in the bridging hydrides: $Cp_4Lu_2(thf)_2(\mu\text{-}H)_2$, 1.98 (6) 2.13 (6) Å; $[Na(thf)_6][Cp_6Lu_2(\mu\text{-}H)]$, 2.09 Å.[10]

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(3) (a) Cotton, F. A.; Schwotzer, W. *J. Am. Chem. Soc.* **1986**, *108*, 4657–4658. (b) Burns, C. J.; Andersen, R. A. *J. Am. Chem. Soc.*, in press.

(4) (a) Andersen, R. A.; Boncella, J. M.; Burns, C. J.; Green, J. C.; Hohl, D.; Rösch, N. *J. Chem. Soc., Chem. Commun.* **1986**, *405*–407. (b) Burns, C. J., unpublished results.

(5) (a) Cook, C. D.; Jauhal, G. S. *J. Am. Chem. Soc.* **1968**, *90*, 1464–1467. (b) Cheng, P. T.; Nyburg, S. C. *Canad. J. Chem.* **1972**, *50*, 912–916.

(6) ${}^{31}P\{{}^1H\}$ NMR of I (C_6D_6, 30 °C, 36.4 MHz) δ 33.0 ($J(PtP) = 3807$ Hz); $(Ph_3P)_2Pt(C_2H_4)$ (C_6D_6, 30 °C, 36.4 MHz) δ 34.0 ($J(PtP) = 3745$ Hz); ${}^1H$ NMR of I (C_6D_6, 30 °C, 500 MHz) δ 7.53 (m), 6.94 (m, Ph H), 2.08 (s Me_5C_5); $(Ph_3P)_2Pt(C_2H_4)$ (C_6D_6, 30 °C, 500 MHz), δ 7.51 (m), 6.94 (m) Ph H), 2.63 ($J(PtH) = 60$ Hz, C_2H_4).

(7) The compound crystallizes in the triclinic space group $P\bar{1}$ with cell dimensions $a = 9.577$ (2) Å, $b = 14.797$ (2) Å, $c = 18.429$ (2) Å, $\alpha = 96.90$ (1)°, $\beta = 92.56$ (1)°, $c = 102.77$ (1)°, $V = 2522$ (1) A^3, $Z = 2$, and d(calcd) = 1.57 g cm^{-3}. The data were collected on a Nonius CAD-4 automated diffractometer with Mo Kα X-rays ($\lambda = 0.71073$ Å) at −80 °C. The structure was solved from Patterson and electron density maps and refined by full-matrix least squares to a conventional R factor of 0.020 ($R_w = 0.031$, and GOF = 1.70) by using 5929 absorption corrected data, where $F_o^2 > 3\sigma(F_o^2)$, against 576 variables. The R valve for all 6568 unique data was 0.026. The non-hydrogen atoms were refined anisotropically. The hydrogen atoms on the ethylene carbons were located in a difference Fourier map and they were refined isotropically. The hydrogen atoms on the phenyl carbons and on the Me_5C_5 ring methyls were located in a difference Fourier map, placed in calculated positions with fixed thermal parameters, and included in structure factor calculations but were not refined.

(8) Tilley, T. D.; Andersen, R. A.; Spencer, B.; Ruben, H.; Zalkin, A.; Templeton, D. H. *Inorg. Chem.* **1980**, *19*, 2999–3003.

(9) (a) Tilley, T. D.; Andersen, R. A.; Zalkin, A., *J. Am. Chem. Soc.* **1982**, *104*, 3725–3727. (b) Tilley, T. D.; Andersen, R. A.; Zalkin, A. *Inorg. Chem.* **1984**, *23*, 2271–2276. (c) Boncella, J. M.; Andersen, R. A. *Organometallics* **1985**, *4*, 205–206. (d) Shannon, R. D. *Acta Crystallogr., Sect. A* **1976**, *32A*, 751–767.

(10) Schumann, H.; Genthe, W.; Hahn, E.; Hossain, M. B.; Van Der Helm, D. *J. Organomet. Chem.* **1986**, *299*, 67–84.

The $Pt(C_2H_4)Yb$ interaction in I is obviously a weak interaction not unlike the d-transition metal olefin–alkali metal interactions found by Jonas and Klein.[11]

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Supplementary Material Available: Tables of atomic positional parameters, thermal parameters, and bond lengths and angles (8 pages). Ordering information is given on any current masthead page.

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(11) (a) Jonas, K. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 47. (b) Brauer, D. J.; Krüger, C.; Roberts, P. J.; Tsui, Y. H. *Ibid.* **1976**, *15*, 48. (c) Goddard, R.; Krüger, C.; Pörschke, K. R.; Wilke, G. *J. Organomet. Chem.* **1986**, *308*, 85–103. (d) Klein, H. F.; Gross, J.; Bassett, J. M.; Schubert, U. *Z. Naturforsch., B* **1980**, *35b*, 614–619. (e) Klein, H. F.; Witty, H.; Schubert, U. *J. Chem. Soc. Chem. Commun.* **1983**, 231–232.

Total Synthesis of (±)-3-Demethoxyerythratidinone: Demonstration of a Radical Cyclization Route to a Site Specific Enol Derivative

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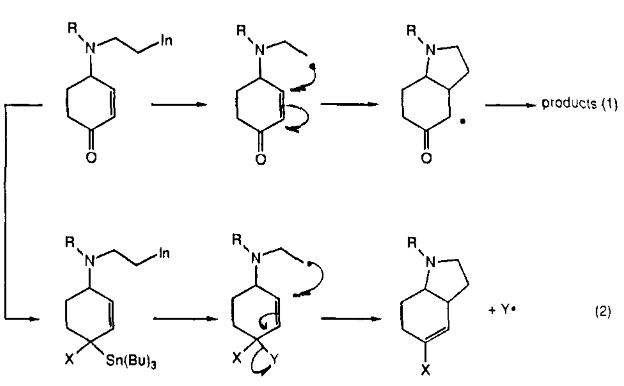
3-Demethoxyerythratidinone (**12**) was isolated from *Erythrina lithosperma* in 1971 by Barton and colleagues.[2a] Though it is structurally one of the simplest of the erythrina alkaloids,[2b] its total synthesis was not achieved until 1984 by Tsuda in several related ways.[3] One of the Tsuda intermediates en route to **12** was the dihydro compound **9**. The conversion[4] of **9** to **12** was accomplished, in ca. 30% yield.

The synthetic studies described herein arose from a convergence of several considerations. It was intended to explore the wider ramifications of a strategem which we first described in 1982[5,6] wherein a β-oxygen-substituted free radical, generated in the presence of a proximate α,β-unsaturated carbonyl system, can cyclize by an intramolecular Giese-type reaction.[7] It was hoped to extend the process to a carbon radical bearing a vicinal nitrogen atom in the connecting chain. This formulation, expressed in eq 1, was in fact realized (vide infra **8** → **9**).

Still more attractive was the possibility of establishing a site-specific enol derivative directly through a free radical cyclization dynamic. The concept is expressed in eq 2. The advantages to be gained from smooth access to regiochemically defined enolate equivalents need not be underscored at this time, since they were well perceived and demonstrated by Stork[8a] and House[8b] many years ago. Hitherto, such systems have been traditionally developed through carbanionic intermediates. In this paper we report the realization of this concept in practice via the use of an allylic geminal acyloxystannane (see sequence **8** → **10** → **11**).[9a,b] This new chemistry is the basis of a remarkably direct synthesis of the titled compound, **12**.



In = radical initiation site ; X = OAc ; Y = Sn(Bu)$_3$

The starting material was the Boc derivative of dopamine dimethyl ether (**1**)[10] which upon bromination ($Br_2/CH_2Cl_2-K_2CO_3$, −78 °C) afforded a 94% yield of the bromo compound **2**,[11] mp 101–103 °C. The potassium salt, generated in situ by the treatment of **2** with potassium hydride in tetrahydrofuran (THF, 25 °C), was converted to its corresponding aryllithium species **2a** by metalation with *n*-BuLi in THF (−78 °C). The other building block was the interesting enone ketal **4**, mp 66–68 °C,[11] obtained (88%) by enol silylation of the commercially available **3** (Me_3SiOTf; Et_3N; CH_2Cl_2) followed by oxidation with palladium(II) acetate (MeCN, 25 °C, 12–14 h).[12]

Coupling of **2a** with **4** (THF, −78 → −30 °C, 8–10 h) afforded the tertiary alcohol **5**[11] in 80–90% yield. The latter underwent a most useful transformation through the action of trimethylsilyl triflate in methylene chloride (−78 °C, 8–10 h). While, in qualitative terms, the formation of **6**[11,13] (mp 169–171 °C) need occasion little surprise, the precise order of steps is not currently known. Treatment of **6** with DBU afforded a 95% yield of the spiro enone, mp 128–130 °C.[7,11] The goal substrate **8**[11] was obtained in 45% yield[14] by the reductive amination of **7** with phenylselenoacetaldehyde **15** (5 equiv) (via sodium cyanoborohydride, 6 equiv, in 1:1 THF–methanol). The directness of this route compensates for the modest yield of the reductive amination.

Treatment of compound **8** with $(n\text{-}Bu)_3SnH$[16] (2–4 equiv, benzene reflux) in the presence of catalytic AIBN (5–10 mol %) led to an 88% yield of **9**.[3] Thus the conjecture embodied in eq 1 has been demonstrated in practice. The internal "Michael-like" free radical cyclization has been demonstrated with a nitrogen

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(2) (a) Barton, D. H. R.; Gunatilaka, A. A. L.; Letcher, R. M.; Lobo, A. M. F. T.; Widdowson, D. A. *J. Chem. Soc., Perkin Trans. 1* **1971**, 874. (b) For recent reviews on erythrina alkaloids, see: Chawla, A. S.; Jackson, A. H. *Nat. Prod. Rep.* **1984**, 371. Dyke, S. F.; Quessy, S. N. In *The Alkaloids: Chemistry and Physiology*; Vol XVIII, chapt. 1, eds. Manske, R. H. F., Rodrigo, R. G. A., Eds.; Academic: New York, 1981; Vol. XVIII, Chapter 1.

(3) Tsuda, Y.; Nakai, A.; Kazo, I.; Suzuki, F.; Haruna, M. *Heterocycles* **1984**, *22*, 1817.

(4) The precise regioselectivity of the sulfenylation reaction which was the first step of the dehydrogenation sequence is not clearly revealed from Tsuda's data.

(5) Danishefsky, S. J.; Chacalamannil, S.; Uang, B.-J. *J. Org. Chem.* **1982**, *47*, 2231. Danishefsy, S.; Taniyama, E.; Webb, R. R. *Tetrahedron Lett.* **1983**, *24*, 11. Danishefsy, S.; Taniyama, E., *Ibid.* **1983**, *24*, 15.

(6) For recent reviews concerning the use of free radical cyclizations in organic synthesis, see: Giese, B., Ed.; Tetrahedron Symposia-in-Print; *Tetrahedron*, **1985**, *41* (19), 3887–4289. Hart, D. *Science* (*Washington, D.C.*) **1984**, *223*, 883.

(7) Giese, B.; Horler, H.; Zwick, W. *Tetrahedron Lett.* **1982**, *23*, 531.

(8) (a) Stork, G.; Darling, S. D. *J. Am. Chem. Soc.* **1964**, *86*, 1761. (b) For a compilation of early studies in this area, see: House, H. O. *Rec. Chem. Prog.* **1967**, *28*, 99.

(9) For recent reports which serve as precedents, see: (a) Padwa, A.; Nimmesgern, H.; Wong, G. S. K. *Tetrahedron Lett.* **1985**, *26*, 957. (b) Keck, G. E.; Enholm, E. J. *Tetrahedron Lett.* **1985**, *26*, 3311.

(10) Tsuda has reported the carbomethoxy version of **10**, see: Tsuda, Y.; Isobe, K.; Toda, J.; Taga, *J. Heterocycl.* **1976**, *5*, 157.

(11) This compound displayed satisfactory ^{1}H NMR (250 or 500 MHz), infrared, MS, and high-resolution mass spectrum.

(12) Ito, Y.; Hirao, T.; Saegusa, T. *J. Org. Chem.* **1978**, *43*, 1011.

(13) Though the stereochemistry of the C5–C6 ring junction (erythrina numbering) of cyclic carbonate **6** was not rigorously proven, ^{1}H NMR (500 MHz) and proton-decoupling experiments fully support the stereochemistry of the ring junction to be cis, as expected.

(14) For reasons that we do not yet understand, the reaction does not go to completion, even with excess reagents. Substantial amounts of pure enone **7**, ca. 20–25%, are recovered. These are not included in the yield.

(15) Toshimitsa, A.; Aoai, S.; Uemura, S.; Okano, M. *J. Org. Chem.* **1980**, *45*, 1953. Toshimitsu, A.; Aoai, T.; Owada, H.; Uemara, S.; Okano, M. *Tetrahedron* **1985**, *41*, 5301.

(16) Cf.: Burke, S. D.; Fobare, W. F.; Armistead, D. M. *J. Org. Chem.* **1982**, *47*, 3348.

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