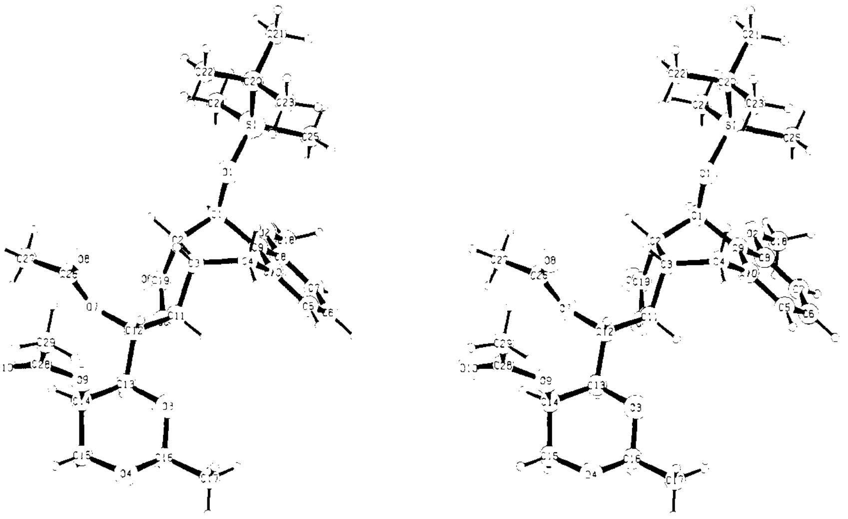

Figure 2. Stereoview of the X-ray structure of lactone **9**.

Table I. Yields of Diels-Alder Adducts

starting material	product (% yield)		selectivity
3	6 (57)	7 (14)	4:1
4	10 (49)	11 (39)	1.2:1
5	12 (68)	13 (17)	4:1[a]

[a] Based on NMR of inseparable mixture.

Ketones **4** and **5** were also successfully condensed with *o*-quinone methide to yield adducts **10**–**13** in good yields (Table I). Evidence that **6**, **10**, and **12** have the identical 3-*S* configuration comes from the nearly identical CD spectra displayed by the products of their BF_3-catalyzed elimination, e.g., **14**. It is clear that the C-3 center is most influential on the CD, because the complementary elimination products derived from **7**, **11**, and **13** displayed CD curves that are the mirror images of those shown by **14**. Thus we can conclude that the face preferences are the same in all our examples, even though the selectivity with ketone **4** is drastically reduced. The sense of preferred addition in our examples of the Diels-Alder reaction not only conform to the predictions of Houk but are also consistent with the results observed by Horton in Diels-Alder reactions of acyclic sugars where the carbonyl of the dienophile is the exo group.[2] On the other hand, our results are opposite in a stereochemical sense to those reported by Liotta[10] for the Diels-Alder addition to dienones with γ-hydroxyl substituents where steric effects seem to be the controlling factor. We can conclude that the use of unsaturated acyclic sugars has great potential for chiral syntheses via Diels-Alder reactions; but caution must be exercised in assuming the sense of asymmetric induction to be obtained.[11]

Supplementary Material Available: Tables of final atomic parameters, final anisotropic thermal parameters, bond lengths, bond angles, and torsion angles (6 pages). Ordering information is given on any current masthead page.

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(9) The crystals were monoclinic, space group $P2_1$, with a = 13.145 (3) Å, b = 7.220 (3) Å c = 17.871 (4) Å, β = 108.10 (2)°, and d_{calcd} = 1.192 g cm^{-3} for Z = 2 ($C_{29}H_{42}O_{10}Si$, M_r = 578.73). The intensity data were measured on a Hilger-Watts diffractometer (Ni-filtered Cu Kα radiation, θ-2θ scans, pulse-height discrimination). The size of the crystal used for data collection was approximately 0.10 × 0.20 × 0.55 mm; the data were corrected for absorption (μ = 10.6 cm^{-1}). A total of 2379 independent reflections were measured for $\theta < 57°$, of which 2096 were considered to be observed $I > 2.5\sigma(I)$. The structure was solved by a multiple-solution procedure (Germain, G.; Main, P.; Woolfson, M. M. *Acta Crystallogr., Sect. A* **1971**, *A27*, 368) and was refined by full-matrix least squares. Six reflections which were strongly affected by extinction were excluded from the final refinement and difference map. In the final refinement, anisotropic thermal parameters were used for the nonhydrogen atoms and isotropic temperature factors were used for the hydrogen atoms. The hydrogen atoms were included in the structure factor calculations but their parameters were not refined. The final discrepancy indexes are R = 0.041 and wR = 0.044 for the remaining 2090 observed reflections. The final difference map has no peaks greater than ±0.3 e Å^{-3}. The absolute configuration is based on the anomalous scattering of the silicon atom and was established by refining both enantiomers. The final weighted R values were 0.0439 for the configuration shown and 0.0449 for its antipode. Thus, by Hamilton's test (Hamilton, W. C. *Acta Crystallogr.* **1965**, *18*, 506) the configuration shown corresponds to the absolute configuration.

(10) Liotta, D.; Saindane, M.; Barnum, C., *J. Am. Chem. Soc.* **1981**, *103*, 3224-3226.

(11) The research at Fordham was supported by Grants CA 27116 and AM 21888. We wish to thank Professor S. M. Weinreb of Penn State University, through whose courtesy several 360-MHz NMR spectra were obtained. We are grateful to Professor T. T. Herskovits of Fordham for the use of this Cary 60 Co instrument and for his assistance in obtaining useful spectra.

Triplet Exciplex Formation in the External Heavy-Atom Effect

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The interaction of an electronically excited aromatic hydrocarbon with a ground-state molecule containing heavy atoms (external heavy-atom effect) has been the subject of a number of recent investigations.[1] Although the nature of the interaction is unresolved, several authors[2] favor a proposal that formation of an excited-state complex or exciplex is involved even though experimental evidence for such an intermediate is meager. In particular, experimental information regarding the external heavy-atom effect upon the triplet states has not required a new intermediate. In this work evidence is presented that strongly argues for a triplet exciplex intermediate in the external heavy-atom interaction of ethyl iodide (EI) with the first triplet of anthracene ($^3A^*$).

EI has been observed to quench A fluorescence with a corresponding enhancement of triplet production.[3] The heavy-atom solvent also causes a decrease in the triplet lifetime of A. Using the technique of flash photolysis to observe triplet-triplet absorption, the triplet-state decay of A in degassed dilute solution ($\sim 10^{-4}$ M) was characterized and studied as a function of EI concentration. A sum of the first-order triplet decay parameters

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(1) (a) Cowan, D. O.; Drisko, R. L. "Elements of Organic Photochemistry"; Plenum Press: New York, 1976. (b) Latas, K. J.; Nishimura, A. M. *J. Phys. Chem.* **1978**, *82*, 491.

(2) (a) DeToma, R. P.; Cowan, D. O. *J. Am. Chem. Soc.* **1975**, *97*, 3291. (b) Thomaz, M. F.; Stevens, B. "Molecular Photochemistry"; Lim, E. C., Ed.; Benjamin: New York, 1969.

(3) DeToma, R. P.; Cowan, D. O. *J. Am. Chem. Soc.* **1975**, *97*, 3283.

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Table I. Summary of the First-Order Triplet Decay Data

	[ferrocene] = 0			[ferrocene] = 2×10^{-7} M		
[EI]	α_0, s^{-1}	α, s^{-1}	$\alpha - \alpha_0$, s^{-1}	α_0, s^{-1}	α', s^{-1}	$\alpha' - \alpha_0$, s^{-1}
0.0	3.8×10^3			4.5×10^3	26.4×10^3	21.9×10^3
0.02	4.0×10^3	5.0×10^3	1.0×10^3	2.6×10^3	28.4×10^3	25.9×10^3
0.05	3.7×10^3	6.1×10^3	2.1×10^3	2.0×10^3	38.6×10^3	36.6×10^3
0.10	3.4×10^3	9.0×10^3	5.6×10^3	12.9×10^3	55.3×10^3	42.4×10^3
0.10				4.2×10^3	47.7×10^3	43.5×10^3

Scheme I. Kinetic Scheme

1	$^3A^* \rightarrow A$	k_{GT}
2	$^3A^* \rightarrow A + h\nu$	k_{PT} $\quad k_{GT} + k_{PT} = \alpha_0$
3	$^3A^* + {}^3A^* \rightarrow 2A$	k_{TT}
4	$^3A^* + Q \rightleftarrows {}^3E^*$	$\overrightarrow{k_{XT}}, \overleftarrow{k_{TX}}$
5	$^3E^* \rightarrow A + Q$	k_{GX}
6	$^3A^* + F \rightarrow A + F$	$k_{G\overline{TF}}$
7	$^3E^* + F \rightarrow A + Q + F$	$k_{G\overline{XF}}$

(α) was obtained from a nonlinear regression fit of the experimental decay traces to a function which contains first- and second-order components as described by DeToma and Cowan.[4] In the presence of the heavy-atom solvent, the first-order triplet decay parameters can be expressed as

$$\alpha = \alpha_0 + k_Q[Q] \tag{1}$$

where k_Q describes the heavy-atom-assisted triplet quenching. The experiments were also performed in solutions containing a fixed concentration (2×10^{-7} M) of ferrocene and as a function of heavy-atom solvent concentration (α'). Methylcyclohexane was used as the solvent.

The values of α, α', and α_0 obtained for each quencher concentration are summarized in Table I. Measurements of the unquenched, first-order decay constant, α_0, was repeated with each quencher concentration run, as a lifetime blank. Variations in the value of α_0 reflect variations in O_2 or other trace impurities present in solution that also quench the A triplet. Although this may introduce some scatter to the data it does not affect the value of $\alpha - \alpha_0$. Plots of $\alpha - \alpha_0$ and $\alpha' - \alpha_0$ as a function of [Q] are shown in Figure 1. From these plots it is evident that the addition of ferrocene, also a triplet quencher of A, introduces a new linearly independent term. This is manifested in the nonzero intercept of the quenching plot. A substantial increase in the slope as a function of Q (= EI) is also observed.

To interpret the results, the simplified kinetic scheme (Scheme I) describing the triplet decay is useful. An initial concentration of anthracene triplets ($^3A^*$) is formed by intersystem crossing from the singlet state following excitation with an intense pulse of light. In addition to first-order processes, the anthracene triplet lifetime is long enough to allow second-order processes to occur. These are accounted for by step 3. Ethyl iodide introduces a pseudo-first-order quenching process. The overall heavy-atom quenching parameter k_Q in the absence of ferrocene, assuming an exciplex mechanism, is given by the expression (steps 4 and 5)

$$k_Q = k_{XT}[k_{GX}/(k_{GX} + k_{TX})] \tag{2}$$

The addition of ferrocene has two effects. First, a linearly independent triplet quenching step, given by step 6 in the kinetic scheme. This is expressed mathematically by the term $k_{G\overline{TF}}[F]$.

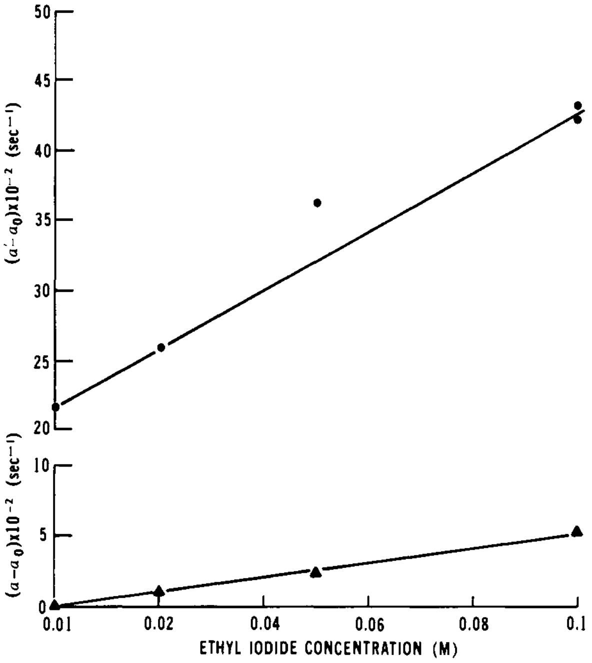

Figure 1. Triplet quenching plot of A by EI in methylcyclohexane solution in the absence of ferrocene ($\alpha - \alpha_0$) and in the presence of ferrocene ($\alpha' - \alpha_0$); r^2 = 0.996 and 0.998, respectively. The point for $\alpha' - \alpha_0$ at 0.05 M EI was not included in the regression analysis.

Second, the exciplex $^3E^*$, which ought to be very close in energy to $^3A^*$, is also quenched by the ferrocene (step 7). This changes the expression for (2)

$$k_Q' = k_{XT}\left(\frac{k_{GX} + k_{G\overline{XF}}[F]}{k_{GX} + k_{TX} + k_{G\overline{XF}}[F]}\right) \tag{3}$$

so that the quenching of the exciplex translates into an increase in the slope of the heavy-atom quenching plot. The values of k_Q and k_Q' obtained from Figure 1 are 53.5×10^2 and 211.6×10^2 M^{-1} s^{-1}, respectively. The condition that $k_Q' > k_Q$ is required by this analysis and was observed in the system investigated. Alternatively, if step 4 were irreversible, not involving an isoenergetic excited-state complex, the presence of the second quencher would have only the effect of an independent molecular triplet quenching step. This mechanism would result in a change in the intercept of the line, but the slope would remain the same.

Ware and co-workers[5] have shown that a two-component decay is not always observed for the monomer when an exciplex is involved, as is the case in this study. The conditions that give rise to this situation are the so-called rapid equilibrium conditions. In the present case, it is reasonable to assume the rapid equilibrium situation since a weakly bound exciplex is expected. Using the value of the intercept from the plot of $\alpha' - \alpha_0$ vs. [Q], one can evaluate $k_{G\overline{TF}} = 10^{10}$ M^{-1} s^{-1}. Since $k_{G\overline{XF}} \approx k_{G\overline{TF}}$, and using simple kinetic analysis, an estimate can be obtained of the equilibrium constant for exciplex formation, $K \approx 7$.[6] If, in addition, one makes the reasonable assumption that the forward reaction, k_{XT}, is of

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[4] Solution of the triplet decay expression

$$-\frac{d_{y\mathrm{T}}(t)}{dt} = \alpha y_{\mathrm{T}}(t) + \beta(\gamma_{\mathrm{T}}(t))^2$$

containing first- and second-order components gives the expression

$$y_{\mathrm{T}}(t) = \left[\left(\frac{1}{y_{\mathrm{T}}(0)} + \frac{\beta}{\alpha}\right)e^{\alpha t} - \frac{\beta}{\alpha}\right]^{-1}$$

for the time-dependent triplet-state concentration, where $y_{\mathrm{T}}(t)$ is the time-dependent optical density of triplet–triplet absorption, and α and β represent the first- and second-order contributions to the triplet decay.

[5] Ware, W. R.; Watt, D.; Holmes, J. D. J. Am. Chem. Soc. **1974**, 96, 7853.

[6] We thank Professor P. J. Wagner for the suggestions that led to the above calculations.

the order of a diffusion-limited process, this and the above value of K are in agreement with the rapid equilibrium situation, which can be expressed, as has been done by Birks:[7]

$$k_{\mathrm{TX}}[\mathrm{Q}] \text{ and } k_{\mathrm{XT}} \gg k_{\mathrm{GT}}, k_{\mathrm{PT}}, k_{\mathrm{GX}}$$

Saltiel et al.[8] have utilized the same concept to present evidence of singlet exciplex formation. They have studied the fluorescence quenching of several aromatic hydrocarbons as a function of quencher concentration in degassed and air-saturated solutions. An increase of the quenching parameter in the presence of O_2 is proposed as evidence of an exciplex intermediate.[9] A related, but less general argument, using a triplet quencher, has been presented by other authors[10] as evidence of a triplet exciplex intermediate in a photochemical reaction. By monitoring the molecular triplet state directly, our experiments provide a method for identifying an exciplex intermediate without the need of a stable reaction product.

We conclude that singlet and triplet exciplex mechanisms for the heavy-atom interactions are consistent with our data and that the reactions cannot proceed solely via simple collisions mechanisms. Also, the use of a second quencher is proposed as a general method for studying short-lived, nonemissive exciplexes in the triplet as well as in the singlet state.

Acknowledgment. Support of this research by the National Science Foundation is gratefully acknowledged.

Registry No. A, 120-12-7; EI, 75-03-6; ferrocine, 102-54-5.

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(7) Birks, J. B. "Photophysics of Aromatic Molecules"; Wiley-Interscience: New York, 1970; pp 309–311.

(8) Charlton, J. L.; Townsend, D. E.; Watson, B. D.; Shannon, P.; Kowalewska, J.; Saltiel, J. *J. Am. Chem. Soc.* **1977**, *99*, 5992 and references therein.

(9) Our studies of the fluorescence quenching of A by EI in degassed and in air-saturated solutions have yielded the relationship $k_{\mathrm{deg}} < k_{\mathrm{air}}$, consistent with an exciplex mechanism in the singlet state. These results will be discussed in a later publication.

(10) See, for example: Gupta, A.; Hammond, G. S. *J. Am Chem. Soc.* **1976**, *98*, 1219. Farid, S.; Hartman, S. E.; Doty, J. C.; Williams, J. R. L. *J. Am. Chem. Soc.* **1975**, *97*, 3697.

Stereocontrolled Synthesis of D-Pentitols, 2-Amino-2-deoxy-D-pentitols, and 2-Deoxy-D-pentitols from D-Glyceraldehyde Acetonide

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In connection with our interest in the marine natural product, palytoxin,[1] it has become necessary to develop a method to transform selectively RCH(OH)CHO into every diastereomer possible for RCH(OH)CH(OH)CH(X)CH$_2$OH. By using the syntheses of D-pentitols, 2-amino-2-deoxy-D-pentitols, and 2-deoxy-D-pentitols from D-glyceraldehyde acetonide as examples, we would like to present a solution to this problem.

D-Glyceraldehyde acetonide (**1**)[2] was converted to the *trans*-allylic alcohol **2**[3] ($[\alpha]_D$ +33.9° (CHCl$_3$, *c* 3.63)) in two steps [(1) (i-PrO)$_2$P(O)CH$_2$CO$_2$Et/t-BuOK/THF/−78 °C and (2) DIBAL/hexane/−78 °C] in 63% overall yield. The stereoselectivity of the modified Wittig reaction was at least 120:1, favoring the trans ester.[4] It was confirmed that loss of optical purity of **1** in this transformation was less than 2%, if any.[5] Sharpless asymmetric epoxidation reaction[6] using (−)-diethyl D-tartrate [t-BuOOH/Ti(i-PrO)$_4$/(−)-DET/CH$_2$Cl$_2$/−23 °C/2 days] yielded a 40:1 mixture[7,8] of the epoxides **4**[3] ($[\alpha]_D$ +38.6° (CHCl$_3$, *c* 1.45)) and **5**[3] ($[\alpha]_D$ −21.5° (CHCl$_3$, *c* 0.77)) in 77% yield. On the contrary, asymmetric epoxidation reaction using (+)-diethyl L-tartrate [t-BuOOH/Ti(i-PrO)$_4$/(+)-DET/CH$_2$Cl$_2$/−23 °C/2 days] yielded a 1:14 mixture[7,8] of the epoxides **4** and **5** in 74% yield. On the basis of observations made by Sharpless,[6] the stereochemistry of the epoxides **4** and **5** was tentatively assigned as indicated and was later confirmed by their successful transformation to pentaacetate of adonitol and pentaacetate of arabitol, respectively (vide infra).

D-Glyceraldehyde acetonide (**1**) was also stereospecifically converted to the *cis*-allylic alcohol **3**[3] ($[\alpha]_D$ +14.0° (CHCl$_3$, *c* 4.52)) in four steps [(1) C$_6$H$_5$HgCCl$_2$Br/(C$_6$H$_5$)$_3$P/C$_6$H$_6$/reflux,[9] (2) n-BuLi/THF/−78 °C followed by MeOCOCl/THF/−78 °C, (3) H$_2$ (1 atm)/Pd–CaCO$_3$/hexane/room temperature, and (4) DIBAL/hexane/−78 °C] in 46% overall yield.[10] The optical purity of **3** was shown to be 98.1%.[5] Sharpless asymmetric epoxidation of **3** using (+)-diethyl L-tartrate proceeded very slowly [t-BuOH/Ti(i-PrO)$_4$/(+)-DET/CH$_2$Cl$_2$/−23 °C/11 days] but yielded a 12:1 mixture[7] of the epoxides **6**[3] ($[\alpha]_D$ −15.6° (CHCl$_3$, *c* 1.03)) and **7**[3] ($[\alpha]_D$ + 11.0° (CHCl$_3$, *c* 1.12)) in 57% yield. On the basis of observations made by Sharpless,[6] the stereochemistry of the epoxides **6** and **7** was tentatively assigned as indicated and was confirmed later from the epoxide ring-opening experiment (vide infra). Asymmetric epoxidation of **3** using (−)-diethyl D-tartrate [t-BuOOH/Ti(i-PrO)$_4$/(−)-DET/CH$_2$Cl$_2$/−23 °C/11 days] yielded a 3:2 mixture[7] of the epoxides **6** and **7** with the unexpected epoxide **6** as the major product. The observed result does not seem to be exceptional for cases of sterically crowded *cis*-allylic alcohols.[11]

The cooperative effect recognized in m-chloroperbenzoic acid (MCPBA) epoxidation of a similar system[12] seemed to have po-

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(1) Uemura, D.; Hirata, Y.; Naoki, H.; Iwashita, T. *Tetrahedron Lett.* **1981**, 2781. Moore, R. E.; Bartolini, G. *J. Am. Chem. Soc.* **1981**, *103*, 2491 and references cited therein.

(2) D-Glyceraldehyde acetonide (**1**) was prepared according to the method reported by H. O. L. Fischer and E. Baer (*Helv. Chim. Acta* **1934**, *17*, 622). If necessary, L-glyceraldehyde acetonide is available; for example, see: M. E. Jung and T. J. Shaw, *J. Am. Chem. Soc.* **1980**, *102*, 6304.

(3) Satisfactory spectroscopic data were obtained for this substance. Spectroscopic data including a copy of the ^{1}H NMR spectrum are included in the supplementary material.

(4) In studies on the synthesis of monensin, we have recognized that the ratio of cis and trans esters in the Horner–Emmons modification of Wittig reaction is sensitive to the structure of phosphonate reagents. In general, a phosphonate reagent with a large phosphonate ester group yields predominantly a trans-α,β-unsaturated ester. Examples are given in footnote 7 of ref 11.

(5) Optical purity of this substance was determined by HPLC analysis [μ-Porasil; ethyl acetate–hexane (1:10)] of the MTPA derivative prepared in four steps [(1) C$_6$H$_5$CH$_2$Br/NaH/DMF/0 °C, (2) 60% aqueous AcOH/room temperature, (3) (Me)$_3$CCOCl/Py/room temperature, and (4) (−)-C$_6$H$_5$C(OMe)(CF$_3$)COCl/Py/room temperature]. No enantiomeric discrimination was observed under the conditions used for this derivatization.

(6) Katsuki, T.; Sharpless, K. B. *J. Am. Chem. Soc.* **1980**, *102*, 5974. The most recent contribution to this method from the Sharpless laboratory is found in: Martin, V. S.; Woodard, S. S.; Katsuki, T.; Yamada, Y.; Ikeda, M.; Sharpless, K. B. *J. Am. Chem. Soc.* **1981**, *103*, 6237; we thank Professor Sharpless for a preprint of this paper.

(7) This ratio was determined by HPLC analysis [μ-Porasil; ether–hexane (1:5)] of the corresponding carbobenzyloxy derivative, prepared by treatment with C$_6$H$_5$CH$_2$OCOCl/Py/THF/−23 °C → room temperature. No diastereomeric discrimination was observed under the conditions used for this transformation.

(8) The difference in the degree of stereoselectivity observed between the cases using (−)-diethyl D-tartrate (unnatural) and (+)-diethyl L-tartrate (natural) might be attributed to the optical purity of the diethyl tartrates themselves or to the effect of the acetonide group existing in the substrate; the $[\alpha]_D$ value of unnatural diethyl tartrate, purchased from Aldrich Chemical, was −8.5° (neat), whereas that of the natural, purchased from Aldrich Chemical, was +7.9° (neat).

(9) Seyferth, D.; Simmons, H. D. Jr.; Singh, G. *J. Organomet. Chem.* **1965**, *3*, 337. Seyferth, D.; Heeren, J. K.; Singh, G.; Grim, S. O.; Hughes, W. B. *J. Organomet. Chem.* **1966**, *5*, 267.

(10) Wittig reaction of D-glyceraldehyde acetonide (**1**) with (C$_6$H$_5$)$_3$P=CHCO$_2$Me in methanol at room temperature gave a 7:1 mixture of cis- and trans-unsaturated esters. The optical purity ($[\alpha]_D$ +129° (CHCl$_3$, *c* 2.63)) of the cis ester obtained by this method was as good as that ($[\alpha]_D$ +127° (CHCl$_3$, *c* 2.38)) obtained from the acetylenic route. Thus, this Wittig reaction provided a short, practical synthesis of **3**: Mitra, A.; Kishi, Y., unpublished results.

(11) Nagaoka, H.; Kishi, Y. *Tetrahedron* **1981**, *37*, 3873.

(12) Johnson, M. R.; Kishi, Y. *Tetrahedron Lett.* **1979**, 4347. Hasan, I.; Kishi, Y. *Ibid.* **1980**, 4229.

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