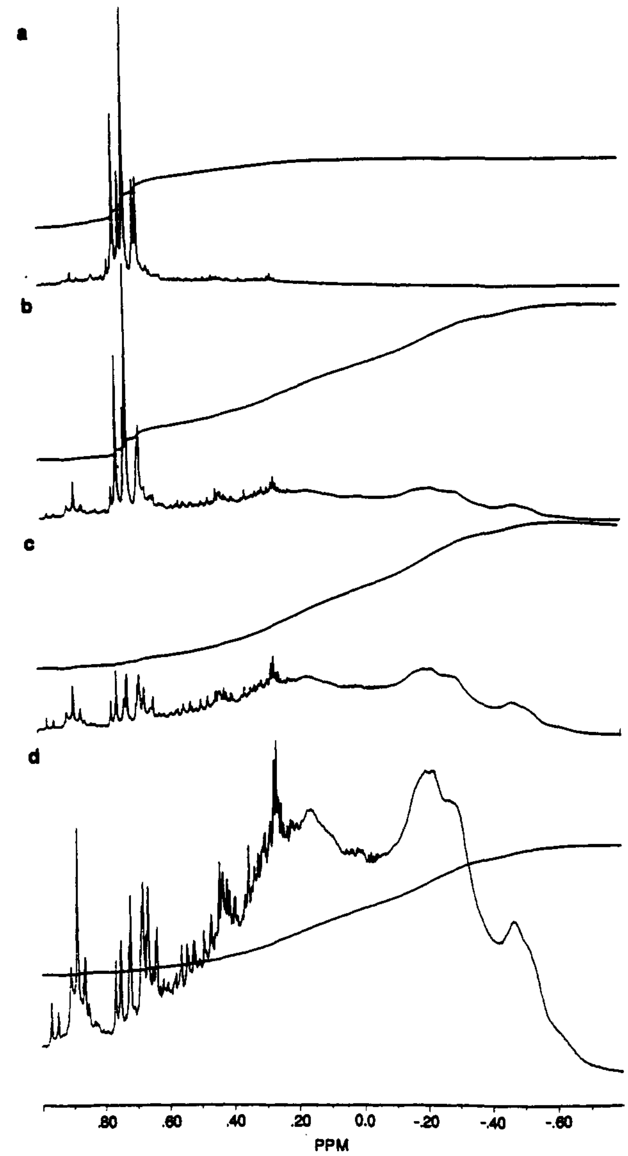

Figure 1. ^1H NMR spectra of the polymerization mixtures of **1** using 1% of $K(SiPh_2)_4K$ as an initiator in benzene-d_6 (a), and after addition of 0.6 vol % THF (b, 25 min; c, 45 min; d, 60 min).

or a decrease in the aggregation of silyl ion pairs in the presence of THF.

Polymerization in a mixture of benzene (40%) and THF (60%) is completed within less than 2 min at the same initiator concentration as shown in Figure 1. However, after 1 h, nearly all polymer has been degraded to cyclopenta- and cyclohexasilanes. Polymerization in pure THF yields only cyclics. Polymerization is completed within seconds in benzene in the presence of equimolar amounts of cryptands ([2.2.2] for silylpotassium and [2.1.1] for butyllithium); however, in contrast to THF, no depolymerization was observed within 24 h. Thus, the polarity and solvation power of a reaction mixture influences propagation, macrocyclization, and termination.

There are three important regions in the methyl group area of the ^1H NMR spectrum. The most deshielded region (>0.6 ppm) corresponds to four-membered rings. The relative reactivities of the isomers must be similar, since the peak intensities do not change during polymerization. The most shielded region (down to −0.6 ppm) corresponds to poly(methylphenylsilylene). Relative intensities of three broad peaks, assigned to iso-, hetero-, and syndiotactic structures,[13] remain similar during polymerization. The sharp signals in the intermediate region are due to cyclopenta- and cyclohexasilanes. At longer reaction times, the characteristic amber color of silyl anions disappears, due to an unidentified termination reaction.

A GPC analysis of polysilanes (based on polystyrene standards[14]) formed by anionic ring-opening polymerization indicates the formation of polymers with molecular weights up to M_{peak} = 100 000 ($M_w/M_n \approx 2$). The highest molecular weights were obtained in the presence of cryptands. Polymerization degrees up to $DP_n \approx 60$ ($M_n \approx 30\,000$) correspond to the $\Delta[M]/[AC^*]$ ratio; lower than expected molecular weights were obtained at higher ratios, probably due to transfer reactions.

Acknowledgment. This work has been supported by the Office of Naval Research. K.M. acknowledges support from the National Science Foundation via the Presidential Young Investigator Award as well as from Eastman Kodak, Hoechst Celanese, PPG Industries, and Xerox Corporation.

Supplementary Material Available: Experimental details for the synthesis of **1** and a typical polymerization procedure (1 page). Ordering information is given on any current masthead page.

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(13) West, R.; Maxka, J. *ACS Symp. Ser.* **1988**, *360*, 6.

(14) de Mahieu, A.-F.; Daoust, D.; Devaux, J. *Bull. Soc. Chim. Belg.* **1989**, *98*, 803.

Stereoselective Aldol Reactions of Chlorotitanium Enolates. An Efficient Method for the Assemblage of Polypropionate-Related Synthons

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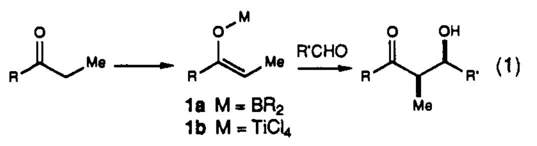
Over the last decade, the stereochemical attributes of the aldol reaction have been improved through the introduction of architecturally refined enolate metal centers.[1] The most efficient of these processes utilizes boron enolates (**1a**, eq 1), which provide a well-ordered transition state leading to predictably high levels of stereoselection. In continuing studies in this area, we have discovered that tetrachlorotitanium enolates (**1b**, eq 1), generated directly from the corresponding ketone or carboxylic acid derivative ($TiCl_4$, R_3N, CH_2Cl_2, −78 or 0 °C),[2,3] participate in highly selective aldol reactions.[4,5] The stereoselectivity in these reactions has been found to be comparable to that reported by us and others for the analogous boron-mediated processes.[6]



(1)

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(1) (a) Evans, D. A.; Nelson, J. V.; Taber, T. *Top. Stereochem.* **1982**, *13*, 1-115. (b) Heathcock, C. H. In *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic Press: New York, 1983; Vol. 3, Chapter 2, pp 111-212.

(2) For leading references to $TiCl_4$–R_3N enolization, see: (a) Lehnert, W. *Tetrahedron Lett.* **1970**, 4723-4724. (b) Harrison, C. R. *Tetrahedron Lett.* **1987**, *28*, 4135-4138. (c) Brocchini, S. J.; Eberle, M.; Lawton, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 5211-5212. This paper, which establishes the precedent that quantitative enolization prior to electrophile introduction can be achieved under similar conditions, was inadvertently not cited in the two previous studies from this laboratory (ref 3).

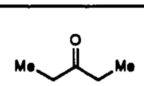
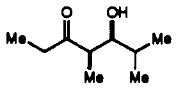
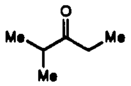
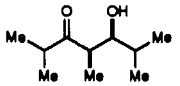
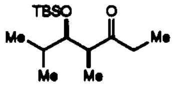
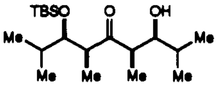
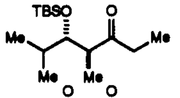
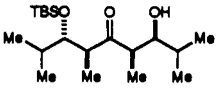
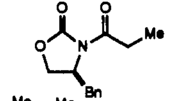
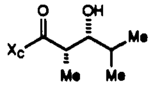
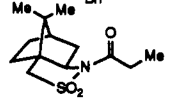
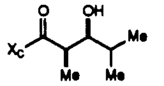
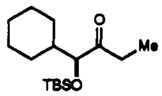
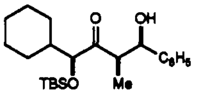
(3) For representative reactions of these enolates, see: (a) Evans, D. A.; Urpí, F.; Somers, T. C.; Clark, J. S.; Bilodeau, M. T. *J. Am. Chem. Soc.* **1990**, *112*, 8215-8216. (b) Evans, D. A.; Clark, J. S.; Metternich, R.; Novack, V. J.; Sheppard, G. S. *J. Am. Chem. Soc.* **1990**, *112*, 866-868.

(4) For leading references, see: (a) Siegel, C.; Thornton, E. R. *J. Am. Chem. Soc.* **1989**, *111*, 5722-5728 and references cited therein. (b) Nakamura, E.; Kuwajima, I. *Tetrahedron Lett.* **1983**, *24*, 3343-3346. (c) Reference 2b.

(5) The studies relating to the characterization of these enolates will be reported at a later time.

0002-7863/91/1513-1047$02.50/0

Table I. Diastereoselective Aldol Reactions of Chlorotitanium versus Dialkylboron Enolates with Isobutyraldehyde[a]

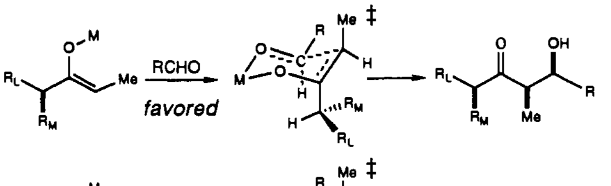
Entry	Substrate	Enolization	Major Product	Yield[b]	Stereoselection[c]
A		TiCl$_4$, *i*-Pr$_2$NEt		95%	92:8 (GLC)
B		TiCl$_4$, Et$_3$N		73%	87:13 (GLC)
C		*n*-Bu$_2$BOTf, *i*-Pr$_2$NEt		61%	>97:3 (NMR)[d]
D		TiCl$_4$, *i*-Pr$_2$NEt		95%	93:7 (GLC)
E		TiCl$_4$, Et$_3$N		94%	92:8 (GLC)
F		9-BBNOTf, *i*-Pr$_2$NEt		57%	94:6 (GLC)
G		TiCl$_4$, *i*-Pr$_2$NEt		96%	96:4 (GLC)
H		TiCl$_4$, Et$_3$N		97%	95:5 (GLC)
I		TiCl$_4$, *i*-Pr$_2$NEt		82%	95:5 (GLC)
J		TiCl$_4$, *i*-Pr$_2$NEt[e]		87%	94:6 (HPLC)[f]
K		TiCl$_4$, TMEDA[e]		84%	98:2 (HPLC)[f]
L		*n*-Bu$_2$BOTf, Et$_3$N		83%	>99:1 (GLC)[g,h]
M		TiCl$_4$, *i*-Pr$_2$NEt[e]		87%	95:5 (NMR)[i]
N		Et$_2$BOTf, *i*-Pr$_2$NEt		82%	97:3 (HPLC)[i,j]
O		TiCl$_4$, *i*-Pr$_2$NEt		81%	99:1 (HPLC)[g]
P		(*c*-C$_5$H$_9$)$_2$BOTf, Et$_3$N		70-85%	98:2 (HPLC)[i,g,k]

[a] All titanium-mediated reactions were performed according to the general titanium aldol procedure (ref. 7). [b] Combined isolated yield of all diastereomers. [c] Diastereoselectivity (ds) was determined by the indicated method (GLC, HPLC, or ^{1}H NMR spectroscopy) and refers to the ratio of the major isomer vs the sum of all other isomers. [d] Reference 6. [e] Enolization was conducted at 0 °C. [f] Two equivalents of aldehyde was required, and the aldol addition reaction was conducted at −78 → 0 °C. [g] Benzaldehyde was used in place of isobutyraldehyde. [h] Reference 11. [i] Five equivalents of aldehyde is required. [j] Reference 12. [k] Reference 10a.

We began our investigations by studying the enolization of isopropyl ethyl ketone. The derived chlorotitanium enolate was generated by the sequential addition of 1.1 equiv of TiCl$_4$ and 1.2 equiv of diisopropylethylamine to a cold (−78 °C) solution of the ketone in CH$_2$Cl$_2$ (0.2 M in ketone, enolization time 30 min). Upon quenching with isobutyraldehyde (1.2 equiv), the syn/anti diastereoselection (syn:anti = 93:7) compared favorably with that obtained through the analogous boron enolate (syn:anti = 94:6), (Table I, entries D–F).

Titanium-mediated aldol reactions of simple unbranched or α-branched ethyl ketones are slightly less selective than their boron counterparts (Table I, entries A–F).[6a,7] However, the isolated yields of syn aldol adducts are frequently higher with the titanium analogues. It is noteworthy that the stereoselectivity of the titanium reactions is modestly dependent on the structure of the amine base (compare entries A vs B, D vs E, G vs H, and J vs K). These results, together with NMR studies to be described at a later time, indicate that these enolates exist as aggregated complexes with the amine intimately associated with the enolate, possibly through ion pairing.

Experiments were conducted to determine the efficiency of these enolates in aldol reactions of chiral ethyl ketones (entries G–I). These cases document instances where efficient enolate asymmetric induction is delivered across the incipient carbonyl functionality. In the illustrated examples, the stereochemical outcome was uniformly excellent, with each case favoring the syn aldol isomer wherein the methyl groups flanking the carbonyl center also possess the syn relationship. In these cases, the major product diastereoisomer is the same as that observed in the boron-mediated aldol process;[8] however, the titanium aldol counterparts were found to be more selective than their boron analogues.[9] A comparison of entries G and I reveals that enolate asymmetric induction evolves from the α-stereocenter, with the β-stereocenter having a negligible effect on the observed stereoselectivity. A uniform steric model for aldol asymmetric induction for both boron and titanium enolates is provided in eqs 2 and 3, where R$_L$ and R$_M$ are the sterically dominant and subordinate substituents, respectively. We speculate that orientation of reacting aldehyde and enolate is such that (A) the enolate substituent, R$_L$, is positioned in an antiperiplanar orientation relative to the forming bond while (B) minimizing the nonbonding interactions between the metal center and the enolate substituents by orienting R$_M$ away from the metal (eq 2). By comparison, the competing transition structure (eq 3) meets condition A but not condition B.[10]



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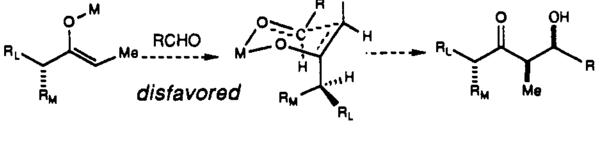

(3)

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(6) (a) Evans, D. A.; Nelson, J. V.; Vogel, E.; Taber, T. R. *J. Am. Chem. Soc.* **1981**, *103*, 3099–3111. (b) See ref 1 for leading references. (c) For a recent reference on the utility of boron enolate derived bond constructions, see: Brown, H. C.; Dhar, R. K.; Bakshi, R. K.; Pandiarajan, P. K.; Singaram, B. *J. Am. Chem. Soc.* **1989**, *111*, 3441–3442 and references cited therein.

(7) General procedure for titanium aldol reactions: TiCl$_4$ (1.1 equiv) is added dropwise to a 0.2 M solution of 1.0 equiv of the ketone or carboxylic acid derivative in CH$_2$Cl$_2$ at −78 °C under N$_2$, giving a yellow slurry. After 2 min, 1.2 equiv of either Et$_3$N or EtN(*i*-Pr)$_2$ is added dropwise, and the resulting deep red solution is stirred at −78 °C under N$_2$ for 1.5 h. After the dropwise addition of isobutyraldehyde (1.2 equiv), stirring is continued at −78 °C for 1.5 h. The reaction is terminated by addition of 1:1 v/v of saturated aqueous NH$_4$Cl, the mixture is warmed to ambient temperature, and the product is isolated by a conventional extraction.

(8) Lithium-mediated aldol reactions of the substrate in entries G and H have been reported to give the alternative syn diastereomer (ds = 76:24); see: McCarthy, P. A.; Kageyama, M. *J. Org. Chem.* **1987**, *52*, 4681–4686.

(9) Paterson, I.; McClure, C. K. *Tetrahedron Lett.* **1987**, *28*, 1229–1232.

The final three examples in Table I illustrate the general utility of titanium enolates in aldol reactions of substrates possessing commonly utilized chiral auxiliaries. Comparative data is provided for the titanium- and boron-mediated aldol reactions of these substrates.[10a,11,12] Entry K is notable in that TMEDA improves the selectivity of this addition for the "nonchelate" product. In each of these reactions, there is no evidence of chelate control in spite of the opportunity for such regulation. The aldehyde stoichiometry was also found to be crucial to the success of these reactions. In most cases (entries A–K, O), only 1.0–1.2 equiv of aldehyde is required for complete consumption of starting material. However, in the case of one substrate (entries J and K), 2 equiv of aldehyde is necessary for complete conversion. With the sultam chiral auxiliary (entries O and P), 5 equiv of aldehyde is required for complete conversion for both the titanium and boron aldol reactions as has been advertised by Oppolzer.[12]

The preceding studies highlight the unexpected stereoselectivity of chlorotitanium enolate aldol bond constructions which offer a practical alternative to the use of other metalloids such as boron to achieve comparable stereocontrol.

Acknowledgment. Support has been provided by the NIH, the NSF, and Merck. The NIH BRS Shared Instrumentation Grant Program (1-S10-RR04870) and the NSF (CHE88-14019) are acknowledged for providing NMR facilities. Postdoctoral fellowships for D.L.R. (American Cancer Society) and F.U. (NATO) are gratefully acknowledged.

Supplementary Material Available: Experimental procedures and spectral data for all new compounds (6 pages). Ordering information is given on any current masthead page.

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(10) Related transition structures have been proposed by others as well: (a) Masamune, S.; Choy, W.; Kerdesky, F. A. J.; Imperiali, B. *J. Am. Chem. Soc.* **1981**, *103*, 1566–1568. (b) Reference 4a. (c) Reference 10. (d) Enders, D.; Lohray, B. B. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 581–583. Variations in the proposed models occur in the disposition of the pendant enolate stereogenic center.

(11) Gage, J. R.; Evans, D. A. *Org. Synth.* **1989**, *68*, 83–91.

(12) Oppolzer, W.; Blagg, J.; Rodriguez, I.; Walther, E. *J. Am. Chem. Soc.* **1990**, *112*, 2767–2772.

The [18] All-Carbon Molecule: Cumulene or Polyacetylene?

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Minneapolis, Minnesota 55455

Received September 24, 1990

A large number of recent experimental[1] and theoretical[2] studies on carbon clusters have mainly focused on their electronic and molecular structures. Small and medium-sized carbon clusters are generally assumed to have linear or monocyclic structures, whereas the larger ones are assumed to be three-dimensional. Recently, the synthesis of the all-carbon molecule C_{18} from an organic precursor was reported.[3] An attempt was also made to determine its electronic and molecular structure by using small-basis ab initio calculations. The SCF results with a 3-21G basis suggest that the cyclic form with alternating bond lengths (acetylenic structure **1**) is the ground-state conformer. Its energy was found to be 53.8 and 37.6 kcal/mol lower than that of other cyclic forms, i.e., the cumulenic structure **2** (perfect D_{18h} symmetry) and the distorted-cumulenic structure **3** (D_{9h} with alternating bond angles), respectively. (The three cyclic forms are all more stable than the linear geometry by several electronvolts.) This prediction is somewhat surprising since the molecule is a $(4n + 2)$ π-electron system, and a structure allowing for the maximum delocalization of the π electrons (i.e., structure **2**) would be expected to be the most stable form.

Table I. Optimized Geometry Parameters of Three Ring Structures: Acetylenic **1**, Cumulenic **2**, and Distorted Cumulenic **3**[a]

structure	symmetry	bond length, Å	bond angle, deg
1	D_{9h}	1.375, 1.194	160
2	D_{18h}	1.277	160
3	D_{9h}	1.277	175, 145

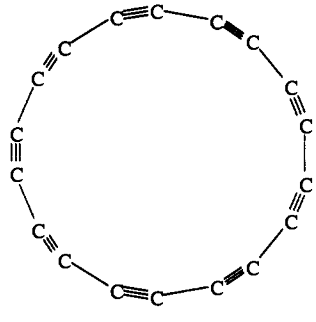
[a] The optimization was made at the MP2 level of theory for **2** and at the SCF level of theory for **1** and **3**, using the [4s3p1d] basis set.

Table II. Energies (kcal/mol) of Alternative Monocyclic Forms of C_{18} Relative to Structure **2**

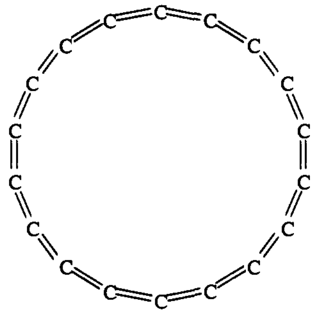
		relative energy	
basis set	method	**1**	**3**
[4s3p1d]	SCF	−68.7	−33.5
[4s3p1d]	36-MP2[a]	54.6	108.8
[5s4p3d2f]	SCF	−71.5	
[5s4p3d2f]	72-MP2[b]	85.7	

[a] Thirty-six valence electrons were correlated. [b] Seventy-two valence electrons were correlated.

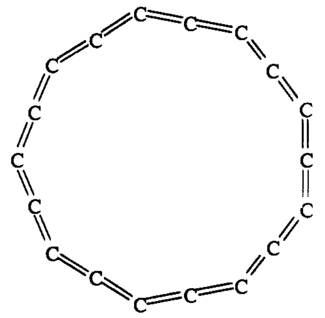
Here, large-basis ab initio SCF and MP2 calculations on the three ring structures **1**–**3** are reported. Geometries were optimized by using a (9s5p)/[4s3p] basis set[4] augmented with a single d



1



2



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(1) Weltner, W., Jr.; Mcleod, D., Jr. *J. Chem. Phys.* **1966**, *45*, 3096. Thompson, K. R.; Dekock, R. L.; Weltner, W., Jr. *J. Am. Chem. Soc.* **1971**, *93*, 4688. Graham, W. R. M.; Dismuke, K. J.; Weltner, W., Jr. *Astrophys. J.* **1976**, *204*, 301. Faibis, A.; Kanter, E. P.; Tack, L. M.; Bakke, E.; Zabransky, B. J. *J. Phys. Chem.* **1987**, *91*, 6645. Van Zee, R. J.; Ferrante, R. F.; Zeringue, K. J.; Weltner, W., Jr.; Ewing, D. W. *J. Chem. Phys.* **1988**, *88*, 3465. Algranati, M.; Feldman, H.; Kella, D.; Malkin, E.; Miklazky, E.; Naaman, R.; Vager, Z.; Zajfman, J. *J. Chem. Phys.* **1989**, *90*, 4617. Cheung, H. M.; Graham, W. R. M. *J. Chem. Phys.* **1989**, *91*, 6664. Vager, Z.; Kanter, E. P. *J. Phys. Chem.* **1989**, *93*, 7745.

(2) Whitside, R. A.; Krishnan, R.; Defrees, D. J.; Pople, J. A.; Schleyer, P. v. R. *Chem. Phys. Lett.* **1981**, *80*, 547. Magers, D. H.; Harrison, R. J.; Bartlett, R. J. *J. Chem. Phys.* **1986**, *84*, 3284. Ritchie, J.; King, H. F.; Young, W. S. *J. Chem. Phys.* **1986**, *85*, 5157. Raghavachari, K.; Whiteside, R. A.; Pople, J. A. *J. Chem. Phys.* **1986**, *85*, 6623. Bernholdt, D. E.; Magers, D. H.; Bartlett, R. J. *J. Chem. Phys.* **1988**, *89*, 3612. Parasuk, V.; Almlöf, J. *J. Chem. Phys.* **1989**, *91*, 1137. Liang, C.; Schafer, H. F., III. *Chem. Phys. Lett.* **1990**, *169*, 150.

(3) Diederich, F.; Rubin, Y.; Knobler, C. B.; Whetten, R. L.; Schriver, K. E.; Houk, K. N.; Li, Y. *Science* **1990**, *245*, 1088.

0002-7863/91/1513-1049$02.50/0