albicans ORF and sequences in databases. No significant DNA similarities were found with sequences contained in GenBank 71 or EMBL. Searches of protein sequence databases (PIR 31 and SWISS-PROT 21) reported a limited similarity to human cholesteryl ester transferase.[12] Significantly greater similarity was obtained by comparing the predicted amino acid sequence of the *C. albicans* oxidosqualene lanosterol-cyclase with the predicted amino acid sequence of the *B. acidocaldarius* squalene hopene-cyclase.[10] Four regions of notable similarity were observed, ranging from 28% identity over 77 residues to 46% identity over 37 residues. Beyond specific sequence identities, both cyclases have regions of primary sequence in which tryptophan and/or tyrosine residues are concentrated. Perhaps the electron-rich aromatic side chains of some of these residues serve to stabilize cationic transition states and/or high-energy intermediates along the cyclization/rearrangement pathway.[13,14]

It has been advanced that the *B. acidocaldarius* cyclase associates with membranes by virtue of its richness in arginine residues.[10] The *C. albicans* cyclase is not arginine-rich. A hydropathy plot indicates that it is a moderately hydrophilic protein with two notable hydrophobic regions (spanning amino acid residues 329-345 and 645-664). These may be involved in anchoring the enzyme to membranes, which would be consistent with the behavior of oxidosqualene cyclase enzymes from plants, mammals, and yeast which reside in the microsomal fractions of cell homogenates and require detergents for their solubilization.[5]

Acknowledgment. This work was supported by Stanford University, a starter grant from the NSF (CHE-9018241), a Camille and Henry Dreyfus Foundation New Faculty Award, a Shell Foundation Faculty Career Initiation Award, and a NSF predoctoral fellowship to C.J.B. We thank Dr. John McCusker and Professor Ronald Davis (Stanford Department of Biochemistry) for helpful discussions, Professor Gregory Verdine (Harvard Department of Chemistry) for supplying the plasmid vector pHN1+, and Bristol-Myers Squibb Pharmaceutical Research Institute for providing plasmids pML18 and pML19.

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Total Synthesis of Angular [4]Phenylene and [5]Phenylene

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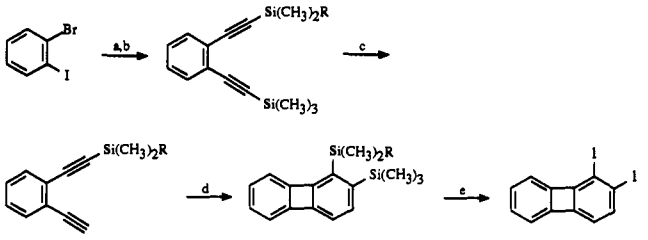
Biphenylene or [2]phenylene, **1**, is a key polycyclic hydrocarbon with which to probe the effect of fusing a classical antiaromatic nucleus, cyclobutadiene, to the aromatic frame of benzene.[1] Activated molecules of this nature are important fundamentally, because their study sheds light on the limits of chemical bonding to carbon and, in a more practical vein, because they are protagonists in current efforts directed toward the elucidation of the mechanism(s) of carcinogenesis by polycyclic benzenoid hydrocarbons,[2] the activation of benzene and related petroleum and coal-derived compounds as a source of industrial raw materials,[3] and the development of organic electroactive materials, such as potential conductors, ferromagnets, memory storage devices, and so on.[4] Connected with these topics is the anticipated novel organometallic chemistry of the strained and electronically reactive π-framework. Finally, the direct connections of the component benzene rings might be exploited in the assembly of the shortest "spacer" analogs of the corresponding acenes, a facet that has already been put to use in the synthesis of biphenylene-bridged porphyrins.[5] The discovery that "CpCo" facilitates the cocyclization of *o*-diethynylarenes with alkynes to generate this otherwise difficult to assemble structural moiety has led to the construction of a number of biphenylenes, as well as several benzocyclobutadienologs, i.e., the linear [3]-, [4]-, and [5]- and the angular [3]phenylene, **2-5**.[6,7]

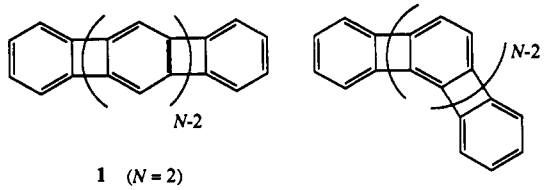
Scheme I[a]



8 **9**

R = $C(CH_3)_2CH(CH_3)_2$

[a] (a) $(CH_3)_3SiC{\equiv}CH$, $PdCl_2[P(C_6H_5)_3]_2$, CuI, $(CH_3CH_2)_3N$, 93%; (b) $(CH_3)_2CHC(CH_3)_2Si(CH_3)_2C{\equiv}CH$,[9] $PdCl_2[P(C_6H_5)_3]_2$, CuI, azacyclohexane, methylbenzene, Δ, 79%; (c) K_2CO_3, CH_3OH, CH_3CH_2OH, 100%; (d) $(CH_3)_3SiC{\equiv}CH$, $CpCo(CO)_2$, 1,3-dimethylbenzene, *hν*, Δ, 19%; (e) ICl, CH_2Cl_2, 0 °C, 56%.



1 (*N* = 2)
2 (*N* = 3)
3 (*N* = 4)
4 (*N* = 5)
5 (*N* = 3)
6 (*N* = 4)
7 (*N* = 5)

In a nutshell, the trends in the physical properties exhibited along the linear series **1-4** appear to strongly indicate complete nonadherence to the Hückel [4*n* + 2] rule, the electronic spectra reflecting a rapidly diminishing HOMO-LUMO gap, and the ^1H

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Table I. Experimental Highest Wavelength UV Bands and Calculated (MMPM) HOMO–LUMO Gaps of Linear and Angular Phenylenes

phenylene	λ_{max} (nm)	HOMO–LUMO gap (eV)
1	363[a,b]	8.53
2	432[c,d]	7.42
3	492[c,e]	6.89
4	530[c,f]	6.60
5	428[c]	8.25
6	448[c]	7.84
7	470[c]	7.73

[a] Isooctane. [b] Reference 1. [c] THF. [d] Reference 2a. [e] Tetrasilyl derivative, reference 2b. [f] Tetrasilyl derivative, reference 2c.

Table II. ^{1}H NMR Data for the Angular Phenylenes **5**, **6**, and **7** in CD_2Cl_2 (δ, ppm; J, Hz)[a]

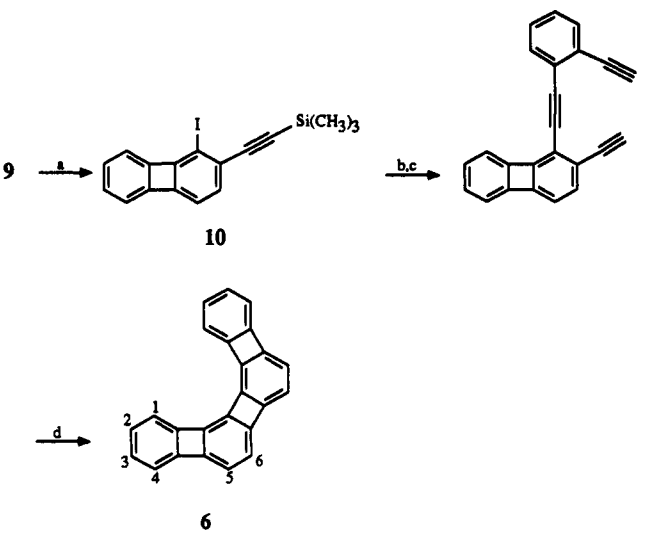
	5	**6**	**7**
δ_{H1}[b]	6.889	6.825	6.871
δ_{H2}[b]	6.991	6.927	6.993
δ_{H3}[b]	6.976	6.939	7.011
δ_{H4}[b]	6.959	6.888	6.934
$\delta_{H5,6}$	6.176[c]	6.312[d,g]	6.294[e,g]
δ_{H7}			6.511[f,g]
^3J(H1–H2)[b]	6.974	6.977	7.019
^4J(H1–H3)[b]	0.836	1.007	0.848
^5J(H1–H4)[b]	1.045	−1.204	1.048
^3J(H2–H3)[b]	8.155	8.110	8.004
^4J(H2–H4)[b]	0.888	0.706	0.804
^3J(H3–H4)[b]	7.057	7.141	7.047

[a] 500 MHz. In CD_2Cl_2, the signals for H5,6 in **6** and **7** are isochronous. [b] Data obtained by simulation using the PANIC program on the Aspect 2000/3000 NMR software management system. [c] ^3J(H5–H6) = 6.53 Hz, ^1J(CH) = 163.70 Hz. [d] ^3J(H5–H6) = 6.68 Hz, ^1J(CH) = 165.18, 162.52 Hz. [e] ^3J(H5–H6) = 6.80 Hz, ^1J(CH) = 163 Hz. [f] ^3J(H7–H8) = 7.00 Hz, ^1J(CH) = 164 Hz. [g] ^3J(HH) obtained from ^{13}C satellite spectrum.

NMR data indicating an increasing degree of paratropism of the internal "benzene" rings. An important question that has awaited an experimental answer is the behavior of the corresponding angular isomers **5**–**7** of **2**–**4**. Recent theoretical work has suggested that, while the linear phenylenes should be more aromatic (on thermodynamic grounds), they might also be more reactive, as indicated by their HOMO–LUMO separation, than the angular systems.[8] We present the first experimental verification of some of these notions by the syntheses of the novel angular phenylenes **6** and **7**, crucial structures as they complement the linear series and, in particular, provide a basis for comparison to **3** and **4**.

The synthetic approach relies on "CpCo" to assemble the aromatic cycles by [2 + 2 + 2] cycloaddition of appropriate alkynes, on Pd to ensure the construction of the required alkynylarene precursors, and on silicon to provide functional group protection and regiocontrol. The key compound **9** (Scheme I) was elaborated as shown in Schemes II and III to the desired targets, intensely yellow **6** and yellow-orange **7**.[10] The most informative physical characteristics of **6** and **7** are found in the UV and ^{1}H NMR data (Tables I and II).

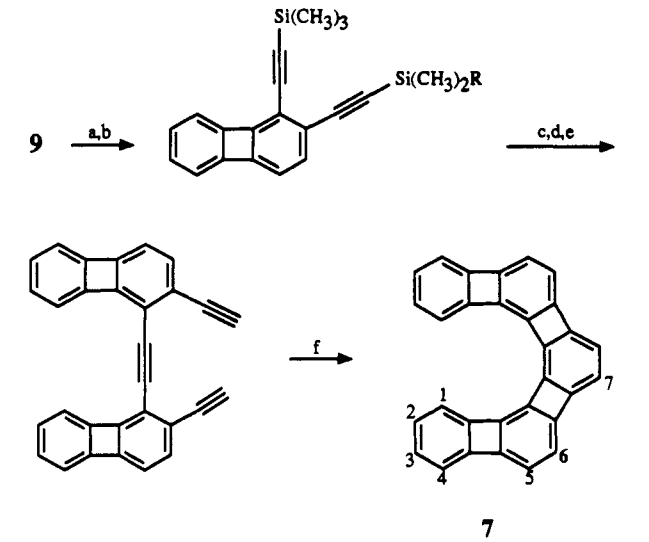
Scheme II[a]



6

[a] (a) $(CH_3)_3SiC{\equiv}CH$, $PdCl_2[P(C_6H_5)_3]_2$, CuI, $(CH_3CH_2)_2N$, 64%; (b) **8**, $PdCl_2[P(C_6H_5)_3]_2$, CuI, $(CH_3CH_2)_3N$, 76%; (c) $(CH_3CH_2CH_2)_4N^+F^-$, oxacyclopentane, 96%; (d) $CpCo(CO)_2$, 1,3-dimethylbenzene, *hν*, Δ, 30%.

Scheme III[a]



7

[a] (a) $(CH_3)_2CHC(CH_3)_2Si(CH_3)_2C{\equiv}CH$, $PdCl_2[P(C_6H_5)_3]_2$, CuI, $(CH_3CH_2)_3N$, 62%; (b) $(CH_3)_3SiC{\equiv}CH$, $PdCl_2[P(C_6H_5)_3]_2$, CuI, $(CH_3CH_2)_3N$, 83%; (c) K_2CO_3, CH_3OH, $(CH_3CH_2)O$, 93%; (d) **10**, $PdCl_2[P(C_6H_5)_3]_2$, CuI, $(CH_3CH_2)_3N$, 58%; (e) $(CH_3CH_2CH_2CH_2)_4N^+F^-$, oxacyclopentane, not isolated; (f) $CpCo(CO)_2$, 1,3-dimethylbenzene, *hν*, Δ, 5%.

As predicted by theory,[8] the HOMO–LUMO gap decreases much less along the angular series compared to its linear counterpart. Most strikingly, the ^{1}H NMR chemical shifts of the "internal" benzene hydrogens (H5,6,7) reveal incremental *deshielding*, in stark contrast to the linear analogs [cf. (C_6D_6) 2,3-bis(trimethylsilyl)biphenylene, δ_{H5} = 6.64 ppm; 2,3,7,8-tetrakis(trimethylsilyl)[3]phenylene, δ_{H5} = 6.23 ppm; 2,3,8,9-tetrakis(trimethylsilyl)[4]phenylene, δ_{H5} = 5.89 ppm; and 2,3,9,10-tetrakis(trimethylsilyl)[5]phenylene, δ_{H6} = 5.56 ppm).[6] It is difficult to provide a rationale for this unusual behavior, a task that constitutes an obvious challenge to theoretical chemists. We propose that the physical properties of the linear phenylenes are governed by the antiaromaticity (hence paratropism) associated with the overriding presence of cyclobutadienoid circuits.[11] On

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(9) (1,1,2-Trimethylpropyl)chlorosilane was a generous gift from Drs. H. Wetter and K. Oertle, Central Research Laboratories, Ciba-Geigy AG, CH-4002 Basel, Switzerland.

(10) All new compounds were found to be pure by spectral and microanalytical analysis. Angular [4]phenylene (**6**): yellow powder, mp 195–202 °C dec; MS (70 eV) *m/z* (rel intensity) 300 (M^+, 100), 272 (9), 149 (31); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 151.1, 149.5, 149.4, 148.8, 138.1, 134.2, 129.0, 128.3, 119.0, 118.1, 115.2, 114.9; IR ($CHCl_3$) 3060, 2940, 1416, 1340, 1114, 1080,1047, 1029, 806, 779, 742, 727 cm^{-1}; UV–vis (THF) λ_{max} (log ϵ) 242 (4.23), 272 (3.73), 285 (3.68), 308 (4.07), 325 (4.29), 402 (3.24), 426 (3.22), 448 (2.72) nm; HRMS calcd for $C_{24}H_{12}$ 300.0939, found 300.0944. Angular [5]phenylene (**7**): orange powder, mp undefined (dec); MS 70 eV) *m/z* (rel intensity) 374 (M^+, 91), 186 (30), 73 (19), 60 (12); ^{13}C NMR (125 MHz, CD_2Cl_2) δ = 151.4, 149.9, 149.6, 149.5, 149.4, 138.4, 137.0, 134.7, 129.7, 128.8, 119.4, 118.6, 116.6, 115.5, 115.3; UV–vis (THF) λ_{max} (log ϵ) 246 (3.93), 326 (3.81), 347 (3.72), 399 (3.14), 422 (3.08), 450 (3.01), 470 (2.54) nm; HRMS calcd for $C_{30}H_{14}$ 374.1096, found 374.1105.

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the other hand, the angular systems are best described by invoking varying (and diminishing) degrees of bond alternation. Thus, **5** contains an internal "cyclohexatriene",[7b] maximizing the "aromaticity" of the flanking two benzene rings. Bond localization is increasingly attenuated along the series **5**, **6**, **7**, as more and more $(4n + 2)$ circuits contribute to the π-structure. Support for this notion is found in the steadily increasing coupling constants between the hydrogens of the internal rings, e.g., **5**, J(H5–H6) = 6.53 Hz; **6**, J(H5–H6) = 6.68 Hz; **7**, J(H5–H6) = 6.80 Hz, J(H7–H8) = 7.00 Hz.

We are actively seeking corroborative evidence for these hypotheses by the continuing investigation of the structural and chemical properties of these unusual molecules.

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1,2-Asymmetric Induction in the Sn–H Bond Insertion Reaction of Aliphatic Fischer Carbene Complex

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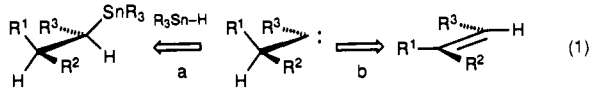
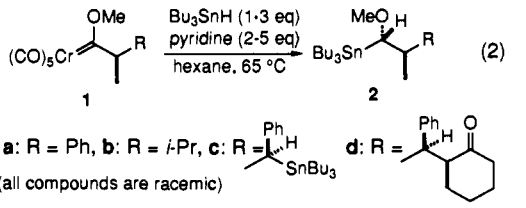
We report herein a case of a novel intermolecular carbene insertion reaction, wherein stereochemical information is effectively transmitted from an adjacent stereogenic center to the reacting carbene carbon (eq 1a). Examples of such 1,2-asymmetric inductions have not been reported previously, perhaps due to the propensity of aliphatic carbenes to undergo 1,2-hydrogen migration (eq 1b) faster than intermolecular insertion.[1]



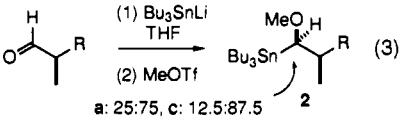
(1)

Aliphatic Fischer carbene complexes readily undergo 1,2-hydrogen migration upon heating with a base.[2] We have found, however, that intermolecular insertion into an Sn–H σ-bond[3] can effectively compete with the intramolecular reaction and that it proceeds with considerable diastereoselectivity for a carbene complex bearing an α-stereogenic center (eq 2). The following example illustrates the experimental procedure, which is very simple. A mixture of carbene complex **1d** (single isomer; 0.147 g, 0.33 mmol), Bu_3SnH (0.26 mL, 0.98 mmol), and pyridine (0.16 mL, 2.0 mmol) was heated in 5 mL of hexane for 8 h at 60 °C. Removal of the yellow precipitate of chromium(0)/pyridine complexes[3] by filtration followed by silica gel chromatography (hexane) gave 145 mg of the α-alkoxytin compound **2d** (81%) as a 93:7 diastereomeric mixture. The reaction gave only a trace amount of an olefin due to 1,2-hydrogen migration.[4]



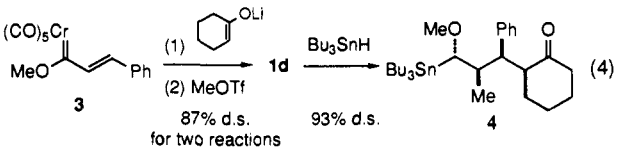
(2)

Inspection of the data in Table I reveals several notable features of the reaction. First, the reaction proceeds with a synthetically useful level (4:1–13:1) of asymmetric induction. Comparison of **1a** and **1c** (entries 1 and 5) with authentic samples (eq 3) indicated that the stereochemistry of these compounds is different from that obtained by Cram addition of Bu_3SnLi to the structurally comparable aldehyde and that the Sn–H insertion and the SnLi addition showed virtually the same level of diastereoselectivity.[5]



(3)

Upon combination with the stereoselective Michael addition/trapping sequence,[6] the insertion reaction stereoselectively creates the four chiral centers in **4** in two steps from **3** (eq 4). The reaction conditions are mild enough not to affect ketone and stannyl groups or to cause epimerization at the carbon adjacent to a ketone group (entries 5 and 6). It is well-known that the conversion of the Sn–C bond in an (α-alkoxyalkyl)stannane to a C–C bond can be carried out with retention of stereochemistry via an (α-alkoxyalkyl)lithium.[7]



(4)

Notably, the diastereoselectivity was little influenced either by the added basic ligand or by the nature of the group 14 metal. Thus, the selectivities of the reaction of **1b** with Bu_3SnH in the presence of pyridine, DABCO, DMAP, Ph_3P, $(PhO)_3P$, and $(MeO)_3P$ fell in a small range, 79, 76, 75, 71, 74, and 74% ds, respectively (40–80%), and the reaction rate remained qualitatively unchanged. In addition, neither the selectivity nor the rate of the reaction changed much for Bu_3SnH and Ph_3SnH (entries 1 and 3), in spite of the apparent difference in their steric demand.[8] The reaction of Bu_3SnD (99% deuterium) with the complex **1a** resulted in complete deuterium incorporation to the carbene center (entry 2),[9] proceeding with selectivity identical with that of the Bu_3SnH reaction. Among other group 14 metals, Ph_3GeH, which was much less reactive (6% yield), also showed a 7:3 selectivity, and $PhMe_2SiH$ gave a complex mixture of products.

While at this time there is insufficient data to discuss the details of the reaction mechanism, Scheme I illustrates some factors relevant to the origin of the diastereoselectivity. In an insertion reaction of a carbene-type reactive intermediate, the stereocontrol is a complex issue, since two new σ-bonds are formed on the forming chiral center in a single reaction. The likely conformation of the 1-phenylethyl complex **1a** is based on the steric bulk of the $Cr(CO)_5$ moiety as supported by MMX calculations.[10] The

(1) For the discussion of this issue, see: Taber, D. F.; Hennessy, M. J.; Louey, J. D. *J. Org. Chem.* **1992**, *57*, 436. Guzman, A.; Pinedo, A.; Saldana, A.; Torre, D.; Muchowski, J. M. *Can. J. Chem.* **1983**, *61*, 454. Cama, L. D.; Cheristensen, B. G. *Tetrahedron Lett.* **1978**, 4233. Padwa, A.; Kulkarni, Y. S.; Zhang, Z. *J. Org. Chem.* **1990**, *55*, 4144.

(2) (a) Casey, C. P.; Anderson, R. L. *J. Chem. Soc., Chem. Commun.* **1975**, 895. Fischer, E. O.; Plabst, D. *Chem. Ber.* **1974**, *107*, 3326. Soderberg, B. C.; Turbeville, M. J. *Organometallics* **1991**, *10*, 3951. (b) General reviews of Fischer carbene chemistry: Wulff, W. D. *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon: Oxford, 1991; Vol. 5, Chapter 9.2.

(3) (a) The insertion reaction of arylcarbene complexes to group 14 hydrides: Connor, J. A.; Rose, P. D.; Turner, R. M. *J. Organomet. Chem.* **1973**, *55*, 111. (b) Mechanistic studies: Connor, J. A.; Day, J. P.; Turner, R. M. *J. Chem. Soc., Dalton Trans.* **1976**, 108. Connor, J. A.; Day, J. P.; Turner, R. M. *J. Chem. Soc., Dalton Trans.* **1976**, 283.

(4) Side reactions involve intramolecular C–H insertion and carbene dimerization, which became dominant for unreactive substrates and metal hydrides (e.g., R_3GeH and R_3SiH).

(5) Further correlation[7] of **2a** to the known diastereomers of 2-phenyl-3-pentanol (EtMgBr + 2-phenylpropanal) confirmed the stereochemistry of **2a** as indicated in eq 3 (see supplementary material).

(6) Cf. Aoki, S.; Fujimura, T.; Nakamura, E. *J. Am. Chem. Soc.* **1992**, *114*, 2985. For diastereoselective aldol chemistry of carbene complexes: Wulff, W. D.; Anderson, B. A.; Toole, A. J. *J. Am. Chem. Soc.* **1989**, *111*, 5485. Dötz, K. H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 587.

(7) Still, W. C.; Sreekumar, C. *J. Am. Chem. Soc.* **1980**, *102*, 1201.

(8) These are consistent with the assumptions made for Scheme I.

(9) There was very small deuterium isotope effect (k_H/k_D = ca. 1.1, competition with 10 equiv each of the hydride and deuteride).

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