vinylcyclopropane **12a** at 60 °C in benzene for 11 h produced hexahydroazulene **10a** in 70% yield. Thermolysis of divinylcyclopropane **12b** under the same conditions was found to produce hexahydroazulene **10b** at a slightly faster rate (60 °C, benzene, 7 h, 97% yield).

$$\mathbf{12a} \xrightarrow[\text{benzene}]{60\,°\text{C}, 11\text{ h}} \mathbf{10a}\ 70\% \tag{2}$$

$$\mathbf{12b} \xrightarrow[\text{benzene}]{60\,°\text{C}, 7\text{ h}} \mathbf{10b}\ 97\% \tag{3}$$

It is clear from these studies that the rates of the intramolecular cyclopropanation process and the subsequent [3,3]-sigmatropic rearrangement are both substituent dependent. The donor–acceptor relationship of the methoxy and carbomethoxy substituents of **3a** and **3b** is likely to be responsible for the rapid rearrangement of these systems to the corresponding 1,4-cycloheptadienes. Further studies of this process and its application to organic synthesis are currently in progress.

Acknowledgment. Support from the Cancer Research Coordinating Committee of the University of California, the donors of the Petroleum Research Fund, administered by the American Chemical Society, the American Cancer Society (Junior Faculty Research Award to D.F.H.), and the National Institutes of Health (GM41984-01) is gratefully acknowledged. The 500-MHz NMR instrument was purchased with assistance from the NIH (RR04733) and NSF (CHE 8814866).

Supplementary Material Available: Experimental procedures and spectral data for **2**, **4a–d**, **5–7**, **8a,b**, **9**, **10a,b**, **11a,b**, and **12a,b** (12 pages). Ordering information is given on any current masthead page.

Asymmetric Induction in Reactions of Styrenes with 1,4-Benzoquinones Utilizing Chiral Ti(IV) Complexes

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The development of new asymmetric reactions is of much current interest, particularly in the realm of carbon–carbon bond forming processes.[1] In this area, the utility of metal complexes incorporating chiral ligands as catalysts for asymmetric carbon–carbon bond construction has considerable appeal, and impressive progress has been made recently in aldol, cycloaddition, and ene reactions and in organometallic addition to carbonyl groups and enones.[2-4] Titanium(IV)-mediated reactions of styrenes and 1,4-benzoquinones result in several different products of formal cycloaddition[5a,b] which can be produced selectively in many cases by proper choice of substituents on the styrene or quinone and/or by careful control of reaction conditions. These reactions are useful in the preparation of biologically interesting pterocarpans,[5c] 2-aryl-2,3-dihydrobenzofurans [e.g., (±)-obtusafuran], and oxidized derivatives [e.g., (±)-kadsurenone].[5d] We now report asymmetric versions of the reactions in which the products are produced in high enantiomeric purity (up to 92% ee). This new methodology should find use in asymmetric syntheses of several classes of biologically active natural products and analogues.

Addition of (2*R*,3*R*)-2,3-*O*-(1-phenylethylidene)-1,1,4,4-tetraphenyl-1,2,3,4-butanetetrol (**4**)[3b] (1 equiv) to a mixture of $TiCl_4$ and $Ti(OiPr)_4$ (1 equiv of each)[6] in CH_2Cl_2 results in an exothermic reaction and produces a complex[7] which promotes the formal cycloaddition of styrenes with 1,4-benzoquinones. The structure of the cycloadduct formed is dependent upon the reaction temperature and substituents on the styrene and the quinone. In most cases, reactions of benzoquinones **2**/**3** with styrenes possessing strong electron-donating groups, **1a**/**b**, at low temperature (−78 or −94 °C) produce mainly the cyclobutane adducts (−)-**5** in good yield and high ee (eq 1 and Table I).[4,8] Styrene **1c** and indene react with quinone **2** to give the 2 + 2 adducts (−)-**5c**/**f**, respectively, in good yields and moderate to high ee. For reasons that are not yet entirely clear, the reaction of **1a** with **3** gives a mixture of **5d** and the 2-aryl-2,3-dihydrobenzofuran **6d**.[9] En-

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(1) (a) *Asymmetric Synthesis*; Morrison, T. D., Ed.; Academic Press: San Diego, 1983/1984; Vols. 2 and 3. (b) Noyori, R.; Takaya, H. *Acc. Chem. Res.* **1990**, *23*, 345. (c) Brown, J. M. *Nature* **1991**, *350*, 191.

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(4) Enantiospecific 2 + 2 cycloaddition reactions of electron-rich alkenes and α,β-unsaturated carbonyl compounds utilizing a complex of Ti(IV) and diol **4** have been reported by Narasaka: (a) Hayashi, Y.; Narasaka, K. *Chem. Lett.* **1990**, 1295. (b) Hayashi, Y.; Niihata, S.; Narasaka, K. *Chem. Lett.* **1990**, 2091. (c) Hayashi, Y.; Narasaka, K. *Chem. Lett* **1989**, 793. (d) Ichikawa, Y.; Narita, A.; Shiozawa, A.; Hayashi, Y.; Narasaka, K. *J. Chem. Soc., Chem. Commun.* **1989**, 1919. The complex[7] formed in the studies reported presently is apparently different from the Narasaka catalyst in that (i) a different stoichiometry of $TiCl_4$–$Ti(OiPr)_4$–diol **4** is required for efficient asymmetric induction[6] and (ii) the Narasaka complex is a true catalyst (≪1 equiv). We have prepared the Narasaka catalyst and successfully reproduced the results reported on asymmetric Diels–Alder reactions.[3b] However, this catalyst fails to promote the cycloaddition reactions of styrenes and quinones, either catalytically or with >1 equiv, and give cycloadducts in enantiomerically enriched form.

(5) (a) Engler, T. A.; Combrink, K. D.; Takusagawa, F. *J. Chem. Soc., Chem. Commun.* **1989**, 1573. (b) Engler, T. A.; Letavic, M. A.; Combrink, K. D.; Takusagawa, F. *J. Org. Chem.* **1990**, *55*, 5810. (c) Engler, T. A.; Reddy, J. P.; Combrink, K. D.; Vander Velde, D. *J. Org. Chem.* **1990**, *55*, 1248. (d) Engler, T. A.; Combrink, K. D.; Ray, J. E. *J. Am. Chem. Soc.* **1988**, *110*, 7931.

(6) The stoichiometry required to obtain a complex that is effective for these asymmetric reactions is critical. A representative experimental procedure is included in the supplementary material. The best ee's are found with (a) a complex prepared from a 1:1:1 ratio of $TiCl_4$, $Ti(OiPr)_4$, and the diol **4**, (b) a ratio of Ti(IV) to the quinone of 5:1, and (c) a complex concentration of ~0.15–0.2 M. The significance of these empirical observations with respect to the mechanism of the reaction and the structure of the active Ti(IV) complex involved[7] is under investigation.

(7) To our knowledge, the solution structures of the Ti(IV) complexes prepared from simple mixtures of $TiCl_4$, $Ti(OiPr)_4$, and added ligands have not been unambiguously established. The system reported herein is complicated additionally by the presence of the quinone as an essential ligand for the Ti(IV). For related studies and discussions, see: Iwasawa, N.; Hayashi, Y.; Sakurai, H.; Narasaka, K. *Chem. Lett.* **1989**, 1581. See also refs 3i and 4 above.

(8) The enantiomeric purity is established by 500-MHz ^{1}H NMR analysis with 5 equiv of (*R*)-(−)-2,2,2-trifluoro-1-(9-anthryl)ethanol as a chiral solvating agent in $CDCl_3$; see: (a) Weisman, G. R. In ref 1, Vol. 1, p 153. (b) Pirkle, W. H.; Hoover, D. J. *Top. Stereochem.* **1982**, *13*, 263. Copies of representative NMR spectra are included in the supplementary material. (c) The recrystallized samples exhibited a constant (for two to three recrystallizations) specific rotation which was in good agreement with the predicted specific rotation calculated from data obtained in the NMR experiments.

(9) (a) Experimental variables that affect the ratio of **5**:**6** formed in these reactions include reaction temperature (vide infra), concentration, and workup procedures. Precipitation of unidentified material is also a complicating factor in some reactions of **1a** with **3** at low temperature. (b) Further experiments regarding these observations are in progress.

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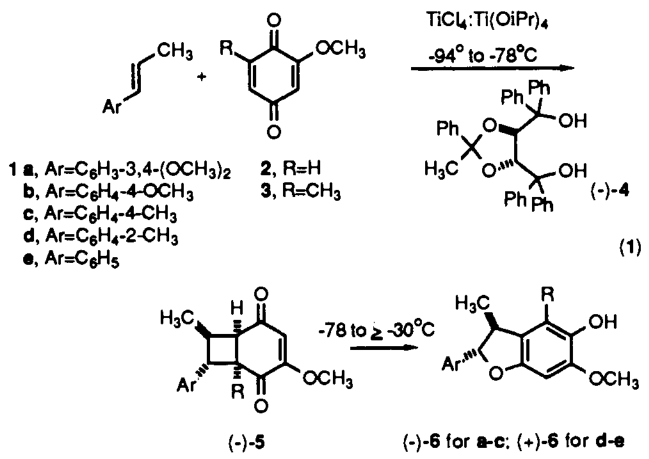
Table I. Asymmetric Reactions of Styrenes and 1,4-Benzoquinones

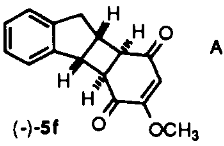
			products			
			5		6	
styrene	quinone	temp, °C	% yield	% ee[a]	% yield (trans:cis)	% ee[a,b]
1a	**2**	−78	88	92	9 (nd)[c]	41
1a	**2**	−78 to rt[d]			95 (15:1)	82
1b	**2**	−94	86	90[e]	10 (nd)[c]	53
1c	**2**	−94	71	86[e]		
1a	**3**	−94 to −78	43	88	49 (>50:1)	83
1a	**3**	−78 to −30			81 (>50:1)	74
1b	**3**	−78	72	90	15 (>50:1)	78
indene	**2**	−78	75	64		

[a] Determined by ^1H NMR; see text. [b] The ee reported is for the trans isomer. [c] Not determined. [d] Room temperature. [e] A 20:1 mixture (by ^1H NMR) of cyclobutane isomers is formed. The major isomer has the structure shown (see ref 5d).

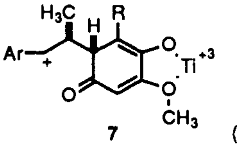
antiomerically pure (−)-**5a,c–f** are obtained by flash chromatography followed by simple recrystallization;[8c] (−)-**5b/c** is obtained as an oil thus far.



For **5/6**: **a**, Ar=C_6H_3-3,4-$(OCH_3)_2$, R=H; **b**, Ar=C_6H_4-4-OCH_3, R=H; **c**, Ar=C_6H_4-4-CH_3, R=H; **d**, Ar=C_6H_3-3,4-$(OCH_3)_2$, R=CH_3; **e**, Ar=C_6H_4-4-OCH_3, R=CH_3.



(−)-**5f**



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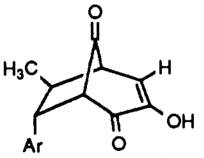
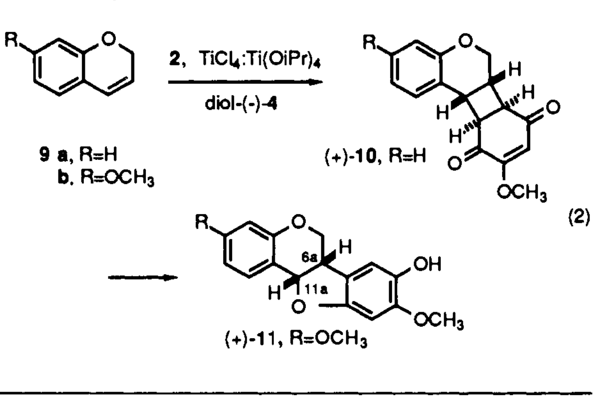


(+)-**8d**, Ar=C_6H_4-2-CH_3
e, Ar=C_6H_5

Rearrangement of (−)-**5a–e** to the 2,3-dihydrobenzofurans **6a–e** is effected by treatment with the chiral complex prepared from $TiCl_4$–$Ti(OiPr)_4$–**4**, as described above, at −78 to −30 °C (for **6d/e**) or to room temperature (for **6a–c**); (−)-**6a–c** and (+)-**6d/e** are all obtained in >79% yield and as mixtures of trans–cis isomers in which the trans predominates (>10:1 for **6b,c,e**; >50:1 for **6a,d**).[10] The rearrangements occur with no loss in enantiomeric purity. Stereochemically pure **6** are obtained by HPLC, flash chromatography, and/or recrystallization. Interestingly, (−)-**6a** and (+)-**6d** can be obtained directly, although in lower enantiomeric purity, from the reaction of **1a** with **2**/**3**, respectively, by allowing the reaction mixture with the chiral Ti(IV) complex to warm to −30 °C (for **6d**) or to room temperature (for **6a**, Table I).[9b] The absolute configurations of (−)-**6a–c** are assigned by comparison of the $[\alpha]_D$ and ORD curves with those reported for similar 2-aryl-2,3-dihydrobenzofurans of known configuration.[11a] The absolute configuration of (+)-**6d** is assigned by conversion to (+)-(*R*)-dimethyl methylsuccinate,[11b] and the configuration of (+)-**6e** is assigned by analogy. Although the sign of the optical rotation for **6a–c** is opposite to that of **6d/e**, the configurations of C-2 and C-3 are the same in **6a–e**. Since it is likely that rearrangement of **5** to **6** involves intermediate **7**,[5] the absolute configurations of (−)-**5a–e** are assigned as shown.

Finally, reactions of quinone **2** with styrenes **1d** and **1e** produce the bicyclo[3.2.1]oct-3-ene-2,8-diones **8d/e**,[5b] respectively, in good yield (61% for both) and with high ee (84 and 90%, respectively).[8] Enantiomerically pure (+)-**8d/e** are obtained by chromatography followed by recrystallization.[8c] The absolute configuration of (+)-**8d/e** has not yet been determined with certainty, although we tentatively assign the configuration as shown from mechanistic considerations.[5]

As an application of this new methodology, the preparation of the naturally occurring pterocarpans was investigated. Reaction of 2*H*-chromene (**9a**) with quinone **2** promoted by the chiral complex[6] gives (+)-**10**[5c] in 86% yield and with 84% ee;[8] again, chromatography and recrystallization give enantiomerically pure (+)-**10**. However, reaction of 7-methoxy-2*H*-chromene (**9b**) with **2** under similar conditions produces the natural pterocarpan (+)-**11**[12] in 77% yield and with 75% ee.[8] Comparison of the optical rotation of **11** prepared in this manner with a sample of the natural product in which the absolute configuration has been assigned as 6a*R*,11a*R* indicates that the synthetic material has the 6a*S*,11a*S* configuration.



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(10) This rearrangement also occurs upon treatment of **5** with protic acids;[5d] however, better yields and material balance were found with the Ti(IV) complex.

(11) (a) For example, 5-hydroxy-6-methoxy-3-methyl-2-phenyl-2(*R*),3-(*R*)-dihydrobenzofuran (obtusafuran) exhibits an $[\alpha]^{25}{}_D = +47°$ ($c = 0.86$, MeOH) and an ORD curve with a positive Cotton effect; see: Gregson, M.; Ollis, W. D.; Redman, B. T.; Sutherland, I. O.; Dietrichs, H. H.; Gottlieb, O. R. *Phytochemistry* **1978**, *17*, 1395. The $[\alpha]^{25}{}_D$ and ORD data for (−)-**6a** are included in the supplementary material. (b) The sequence (1) hydrogenolysis (H_2, Pd/C) of the dihydrobenzofuran nucleus, (2) exhaustive ozonolysis (O_3, HOAc) with oxidative workup (H_2O_2, H_2O), and (3) diazomethane esterification (CH_2N_2, Et_2O) was used. For procedures and $[\alpha]_D$ values of the (*R*)-(+)-methylsuccinic acid and (*R*)-(+)-dimethyl methylsuccinate, see ref 11a and: Hayashi, T.; Yamamoto, A.; Hagihara, T. *J. Org. Chem.* **1986**, *51*, 723.

(12) Bezuidenhoudt, B. C. B.; Brandt, E. V.; Ferreira, D. *Phytochemistry* **1987**, *26*, 531. A sample of (−)-**11** was kindly provided by Professor Ferriera: natural **11**, $[\alpha]^{23}{}_D = -155°$ (c = 5.3 mg/mL, $CHCl_3$); synthetic **11**, $\alpha^{23}{}_D$ = +123.7° (c = 23 mg/mL, $CHCl_3$).

In summary, 8-arylbicyclo[4.2.0]octenediones, 2-aryl-2,3-dihydrobenzofurans, and/or 7-arylbicyclo[3.2.1]octenediones are formed enantiospecifically in reactions of various styrenes with quinones promoted by Ti(IV) complexes incorporating chiral ligands. The reactions are notable in that, to our knowledge, (a) these are the only direct, enantiospecific routes to ring systems of this type; (b) these include the first examples of asymmetric 5 + 2 cycloadditions promoted by an external chiral metal complex; and (c) they provide additional examples of asymmetric cyclobutane syntheses utilizing external chiral metal complexes.[4] In addition, four new contiguous asymmetric centers are formed in a single reaction.

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Supplementary Material Available: Representative experimental procedures for the preparation of **5**, **6**, **8**, and **11** in asymmetric form, selected physical and spectral data for (−)-**5**, (−)-**6a–c**, (+)-**6d/e**, (+)-**8d/e**, and (+)-**10** and full spectral data for the corresponding racemates, representative examples of NMR spectra used to establish % ee's, and summary of NOE data used to establish the stereochemistry of **5** (43 pages). Ordering information is given on any current masthead page.

Contribution of Nonbonded Interactions to the Destabilization of a Group 14 Bicyclo[1.1.1]pentane

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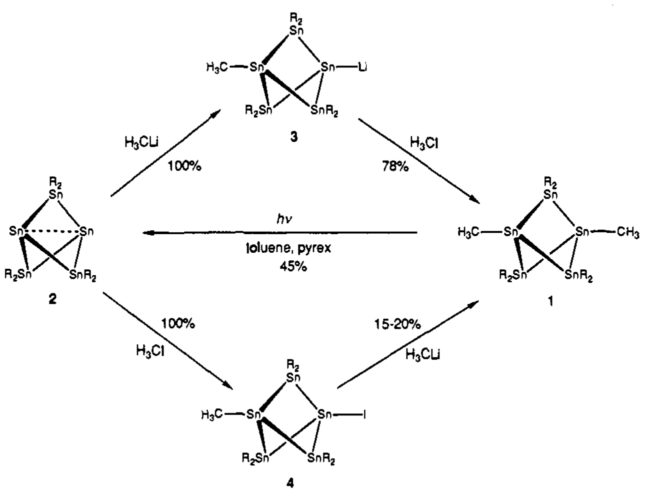
A current goal of group 14 chemistry is to develop modern structural theories for the heavier elements that can rival that for carbon in their ability to reliably predict stable and metastable atomic configurations on the potential energy surface of a given molecular system. In recent years, one approach toward this objective has been to obtain experimental structural parameters from the solid-state structures of a number of topologically interesting polycyclic compounds that possess M–M bonded frameworks (M = Si, Ge, and Sn) and to correlate them with the values predicted by molecular orbital calculations.[1,2] From these studies, it is now recognized that, while the correlation is generally high, nonbonded interactions between the bulky substituents used to "kinetically stabilize" synthetic derivatives can significantly contribute to structural discrepancies.[1e,2a] Herein, we report the synthesis of a bicyclo[1.1.1]pentastannane derivative, **1**, by two complementary routes, and its anomalous chemical and spectroscopic behavior, which further reveals how nonbonded interactions in synthetic derivatives of heavy-atom polycyclic compounds can influence another feature of theoretical interest, stability.

Scheme I[a]



[a] R = 2,6-diethylphenyl.

Synthesis of 1.[3] Addition of methyllithium (1 equiv) to a solution of 2,2,4,4,5,5-hexakis(2,6-diethylphenyl)pentastanna[1.1.1]propellane (**2**)[2j,k] in *n*-pentane quantitatively produces the adduct **3**, which can be isolated as an unstable pale-yellow crystalline material by cooling the reaction mixture to −40 °C (Scheme I). If, however, excess iodomethane is added to the initially formed solution of **3**, compound **1** can be obtained in a 78% overall yield. Alternatively, **1** can be produced by the addition of methyllithium to the 1-iodo-3-methylbicyclo[1.1.1]pentastannane derivative **4**,[2k] albeit in much lower yield (<20%) (Scheme I). With isotopically labeled reagents, this synthetic methodology has been used to prepare $[1\text{-}^{13}CH_3,99\%]$-**1** (**1a**) and $[1,3\text{-}^{13}CH_3,99\%]$-**1** (**1b**) as well.

Properties of 1. Compound **1** is an air-sensitive, yellow crystalline material which displays reversible thermochromic behavior by being nearly colorless at 77 K in a glass matrix (3-methylpentane) and in the solid state.[3] This observation correlates well with variable-temperature electronic spectra, which reveal that an absorption maximum, attributable to a $\sigma \rightarrow \sigma^*$ transition of the Sn–Sn bonded framework of **1**,[4] undergoes an apparent hypsochromic shift from 390 nm (ϵ 1000) at room temperature to 370 nm at 20 K. In the dark, solutions of **1** are indefinitely stable;[5] however, these solutions are sensitive to light, and quite

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(3) Detailed information is supplied in the supplementary material.

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