Table I. GPC Data for Isocyanate Block Copolymerizations

entry	isocyanate 1	isocyanate 2	M_n after 1[a]	M_n after 1 + 2[a]
1[b]	*n*-hexyl	*n*-hexyl	42 500	119 500
2[c]	*n*-hexyl	*n*-butyl	46 400	155 200
3[c]	*n*-hexyl	*n*-hexyl	46 400	193 300

[a] Determined by GPC relative to polystyrene standards. [b] Without isolation of the polymer plus end-group. [c] With isolation of the polymer plus end-group.

groups intact. Our current proposed mechanism involves coordination and insertion of the isocyanate monomer into a titanium–amidate end-group species.[12] The ability to isolate a polymer with its active end-groups in linear chain-growth polymerizations is quite rare,[13] provides opportunities for studying the polymerization in greater detail, and expands the synthetic usefulness of this polymerization. For example, this "polymeric reagent" can be manipulated in its solid form and redissolved at a later date for use in depolymerization kinetics or for the synthesis of isocyanate–isocyanate block copolymers (vide infra).

The equilibrium behavior of this polymerization ($K_{eq} = 2$, at ~30 °C) affords a method for measuring the governing solution thermodynamics. Measurement of the variation in the equilibrium constant of the polymerization versus temperature (*n*-hexyl isocyanate, range 20–80 °C) yielded $\Delta H_p = -8.8$ kcal/mol, $\Delta S_p = -28$ cal/(mol·K), and $T_c = 43.4$ °C[14] (T_c for $[M]_e = 1$ M; corrections for the variation in the activity of the monomer due to the presence of high polymer were neglected).[15] It is noted that T_c is quite low (between those found for chloral (13 °C) and α-methylstyrene (66 °C) polymerizations)[16] and is consistent with the known degree of steric interactions in linear alkyl isocyanate polymers.[17] As expected, cleavage of the active end-group from the polymer chain (methanol wash) results in the expected thermally robust polymer with a decomposition temperature near 200 °C.[10b] In summary, high yields of polymer can be obtained by either (1) decreasing the amount of solvent used (in the limit, a bulk polymerization) or (2) reducing the reaction temperature.

The "living" behavior of this polymerization was demonstrated by several experiments.[18] In a "living" polymerization, M_n should vary as a linear function of the monomer to initiator ratio, and we observe this behavior when using I or II (Figure 1). Also, M_n should vary linearly with the percent conversion of the reaction, which is also observed in these polymerizations (Figure 2).

The titanium end-groups stay active throughout the polymerization until quenched by the addition of protic sources. This is demonstrated by the fact that the polymer chains can be polymerized and depolymerized at will by addition of monomer or solvent, respectively. GPC traces showed no bimodal distributions of molecular weights when fresh monomer was added to a solution of active polymer. Such distributions would indicate that termination or transfer processes had occurred (Table I, entry 1).

The robust nature of the titanium–amidate end-groups can be exploited in the synthesis of block copolymers. Isocyanate–isocyanate block copolymers were prepared by isolating the polymer possessing the titanium end-groups and subsequently redissolving this "active" polymer in the presence of another (or the same) monomer. Several isocyanate blocks were prepared using this method; no bimodal distributions of molecular weights were observed via GPC (Table I, entries 2 and 3).

Finally, the polydispersities of the product polymers range from 1.1 to 1.3. (These values are based on GPC data calibrated relative to the M_v of samples used in this paper and should only be considered approximate.) We are currently studying the kinetics and mechanism of this polymerization and are synthesizing active species analogues.

Acknowledgment. This work was supported by University of California "Start-up Funds" and a generous contribution from E. I. du Pont de Nemours and Company. T.E.P. gratefully acknowledges the Department of Defense for a NDSEG Fellowship.

Supplementary Material Available: Experimental procedures for all polymerizations with characterization techniques and data (3 pages). Ordering information is given on any current masthead page.

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[12] This was based on known chemistry of titanium–oxygen, –nitrogen, and –carbon bonds with isocyanates. Some pertinent sources for Ti(IV) and Zr(IV) are the following: (a) Chandra, G.; Lappert, M. F. *Inorg. Nucl. Chem. Lett.* **1965**, *1*, 83. (b) Meth-Cohn, O.; Thorpe, D.; Twitchett, H. J. *J. Chem. Soc. C* **1970**, 132. (c) Clark, R. J. H.; Stockwell, J. A.; Wilkins, J. D. *J. Chem. Soc., Dalton Trans.* **1976**, 120. (d) Gambarotta, S.; Strologo, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Inorg. Chem.* **1985**, *24*, 654. Also $TiCl_4$, alone, will not polymerize isocyanates.

[13] Gilliom, L. R.; Grubbs, R. H. *J. Am. Chem. Soc.* **1986**, *108*, 733.

[14] A previous report of T_c for poly(*n*-hexyl isocyanate) listed $T_c = -22$ °C. Ivin, K. J. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 487.

[15] Szwarc, M. *Adv. Polym. Sci.* **1983**, *49*, Chapters 2 and 3.

[16] Allcock, H. R.; Lampe, F. W. *Contemporary Polymer Chemistry*; Prentice Hall: Englewood Cliffs, NJ, 1990; Chapter 10.

[17] Cook, R.; Johnson, R. D.; Wade, C. G.; O'Leary, D. J.; Munoz, B.; Green, M. M. *Macromolecules* **1990**, *23*, 3454.

[18] Sources for an overview and criteria of living polymerizations: (a) Szwarc, M.; Levy, M.; Milkovich, R. *J. Am. Chem. Soc.* **1956**, *78*, 2656. (b) Szwarc, M. *Nature* **1956**, *178*, 1168. (c) Flory, P. J. *J. Am. Chem. Soc.* **1940**, *62*, 1561. (d) van Beylen, M.; Bywater, S.; Smets, G.; Szwarc, M.; Worsfold, D. J. *Adv. Polym. Sci.* **1988**, *86*, 87. (e) Gold, L. *J. Chem. Phys.* **1958**, *28*, 91. (f) Fetters, L. J. Monodisperse Polymers. In *Encyclopedia of Polymer Science and Engineering*, 2nd ed.; Wiley-Interscience: New York, 1987; Vol. 10, p 19.

Cyclization Reactions of a Molybdenum Carbene Complex with 1,3-Nonadien-8-ynes

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Recently we have demonstrated that alkyl methoxy molybdenum carbene complexes will readily produce substituted cyclopropanes when treated with electron-poor olefins.[1] This cyclopropanation process was found to occur under milder conditions and at a faster rate than the analogous process with chromium- and tungsten-derived complexes. We have also demonstrated that, when an alkyne is tethered to the molybdenum carbene complex, vinylcarbene complexes can be generated in situ and trapped by the cyclopropanation of electron-poor olefins to give vinylcyclopropanes in good yield.[2] As part of a project directed toward the development of transition-metal-mediated approaches to polycyclic systems, we report herein the reactivity of 1,3-nonadien-8-ynes with butyl methoxy molybdenum carbene complex **1a**.

On the basis of previous studies by ourselves[1-3] and others,[4] it was anticipated that treatment of dienyne **2**[5] with molybdenum

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[1] (a) Harvey, D. F.; Brown, M. F. *Tetrahedron Lett.* **1990**, *31*, 2529–2932. (b) For an earlier report of the cyclopropanation of electron-poor olefins with [phenyl(methoxy)carbene]pentacarbonylmolybdenum(0), see: Dötz, K. H.; Fischer, E. O. *Chem. Ber.* **1972**, *105*, 1356–1367.

[2] Harvey, D. F.; Brown, M. F. *J. Am. Chem. Soc.* **1990**, *112*, 7806–7807.

[3] Harvey, D. F.; Lund, K. P.; Neil, D. A., manuscript in preparation.

[4] (a) Wienand, A.; Reissig, H.-U. *Tetrahedron Lett.* **1988**, *29*, 2315–2318. (b) Ressig, H. U.; Buchert, M. *Tetrahedron Lett.* **1988**, *29*, 2319–2320. (c) Wulff, W. D.; Banta, W. E.; Kaesler, R. W.; Lankford, P. J.; Miller, R. A.; Murray, C. K.; Yang, D. C. *J. Am. Chem. Soc.* **1990**, *112*, 3642–3659. (d) Wulff, W. D.; Kaesler, R. W. *Organometallics* **1985**, *4*, 1461–1463. (e) Casey, C. P.; Hornung, N. L.; Kosar, W. P. *J. Am. Chem. Soc.* **1987**, *109*, 4908–4916. (f) Hoye, T. R.; Rehberg, G. M. *J. Am. Chem. Soc.* **1990**, *112*, 2841–2842. (g) Hoye, T. R.; Rehberg, G. M. *Organometallics* **1989**, *8*, 2070–2071. (h) Hoye, T. R.; Korkowski, P. F.; Rydberg, D. B. *J. Am. Chem. Soc.* **1988**, *110*, 2676–2678. (i) Rudler, H.; Parlier, A.; Yefsah, R.; Denise, B.; Daran, J. C.; Vaissermann, J.; Knobler, C. *J. Organomet. Chem.* **1988**, *358*, 245–272. (j) Wienand, A.; Reissig, H.-U. *Organometallics* **1990**, *9*, 3133–3142.

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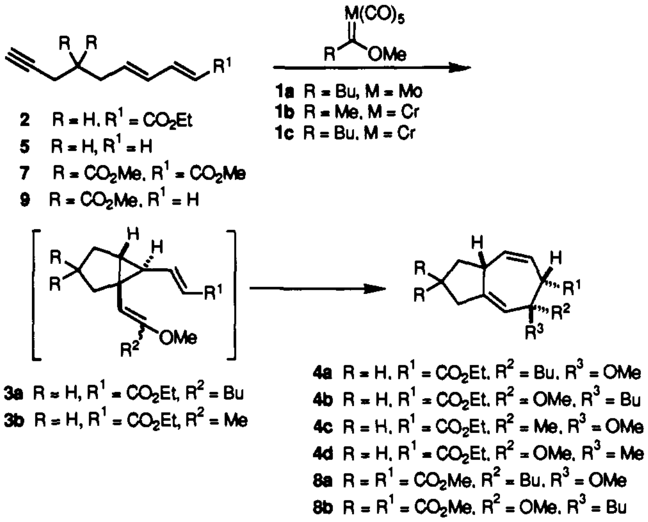
Scheme I



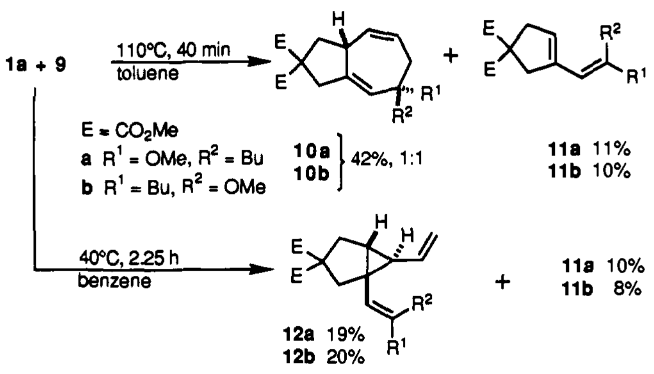
carbene complex **1a** would lead to divinylcyclopropane **3**. Under the reaction conditions, **3** would be expected to undergo [3,3]-sigmatropic rearrangement to give bicyclo[5.3.0]decane **4** (see Scheme I). Indeed, in the event, treatment of **2** with **1a** in benzene at 60 °C for 0.5 h gave hexahydroazulenes **4a** and **4b** (1:4.8 ratio) in a combined 87% yield. Divinylcyclopropanes **3a** and **3b** were not observed under these or any other conditions tried with dienyne **2**. This cyclization process represents a very rapid entry into the bicyclo[5.3.0]decane ring system found in a wide variety of biologically active natural products.[6]

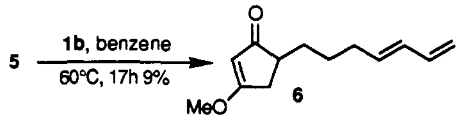
In this cyclization process the molybdenum-based system was found to be far superior to the analogous chromium complex. For example, treatment of dienyne **2** with methyl methoxy chromium complex **1b** (benzene, 60 °C, 1.5 h) produced hexahydroazulenes **4c** and **4d** in a 1.2:1 ratio in 24% yield. Butyl methoxy complex **1c** (benzene, 80 °C, 50 min) gave a 1.2:1 ratio of **4a** and **4b** in 22% yield. The chromium-based reactions required higher temperature or longer reaction time in order for starting material to be completely consumed.

The divinylcyclopropane rearrangement of **3a** to **4a,b** and **3b** to **4c,d** is expected to proceed through a boat transition state producing only a single stereogenic relationship between C_4 and C_7.[7] The isomeric mixture at C_3 is therefore thought to reflect the ratio of enol ether isomers at the divinylcyclopropane stage. Isomers **4a,c** arise from the (*Z*)-enol ether of **3** while **4b,d** are formed from the (*E*)-enol ether of **3**.

Cyclization of dienyne **5**,[5] lacking the electron-withdrawing carbethoxy group on the diene, was also investigated. It failed to give any of the desired hexahydroazulene cyclization product with either molybdenum carbene complex **1a** or chromium complex **1b**. The only isolable product obtained, under our cyclization conditions (vide supra), was cyclopentenone **6** from treatment of **5** with chromium carbene complex **1b**. This cyclopentenone formation process has recently been described by Wulff and coworkers and is derived from a vinylketene intermediate produced by the insertion of CO into the in situ generated vinylcarbene complex.[8] No isolable products were obtained when dienyne **5** was treated with molybdenum carbene complex **1a**. The failure of substrate **5** to participate in the desired cyclization process can be attributed to the absence of the electron-withdrawing carbethoxy group on the 1,3-diene.

Scheme II





(1)

Previous studies of cyclizations of group VI carbene complexes with enyne substrates have demonstrated that related cyclizations proceed smoothly when *gem*-carbomethoxy groups are situated on the tether between the alkyne and the alkene.[4f–h] We believe that the success of these reactions is related to the *gem*-dialkyl effect of the substituents on the tether.[9] To probe this issue in our system, dienynes **7**[5] and **9**,[5] containing *gem*-carbomethoxy groups on the tether, were prepared and their reactivity with complex **1a** was investigated.

Treatment of dienyne **7**[5] with molybdenum carbene complex **1a** (THF, 60 °C, 1 h) proceeded smoothly to give hexahydroazulenes **8a** (36%) and **8b** (45%). The success of this cyclization was expected since, with the electron-withdrawing group on the diene (substrate **2**), cyclization had been observed to proceed well (vide supra).

Dienyne **9** represents a more critical test of the *gem*-dialkyl effect. This substrate contains the *gem*-carbomethoxy groups on the tether but lacks the electron-withdrawing group on the 1,3-diene. Treatment of molybdenum complex **1a** with dienyne **9** at 110 °C for 40 min produced a 1:1 mixture of the desired hexahydroazulenes **10a** and **10b** (42%) accompanied by dienes **11a** (11%) and **11b** (10%) (Scheme II). Dienes **11a,b** are the result of the in situ generated vinylcarbene complex undergoing an olefin metathesis reaction with the tethered 1,3-diene. Thus, the desired carbene-mediated cyclization process can be induced either by the presence of an electron-withdrawing group on the diene or by appropriate substituents on the tether between the alkyne and the diene.

When dienyne **9** was treated with **1a** at lower temperature (40 °C, 2.25 h), divinylcyclopropanes **12a** (19%) and **12b** (20%) were isolated along with metathesis products **11a** (10%) and **11b** (8%). Hexahydroazulenes **10a** and **10b** were not observed under these milder conditions. The isolation of **12** from this reaction confirmed our hypothesis (vide supra) that divinylcyclopropanes are indeed intermediates in this cyclization pathway.

The absence of **10a,b** under these milder cyclization conditions was surprising since most divinylcyclopropanes have been found to smoothly rearrange to the corresponding 1,4-cycloheptadienes at room temperature or below.[10] Indeed, thermolysis of di-

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(5) Dienynes **2**, **5**, **7**, and **9** were prepared from readily available substrates by using standard synthetic procedures. Experimental details are provided in the supplementary material.

(6) For reviews, see: (a) Heathcock, C. H. In *Total Synthesis of Natural Products*; ApSimon, J., Ed.; John Wiley and Sons, Inc.: New York, 1973; Vol. 2, p 197. (b) Heathcock, C. H.; Graham, S. L.; Pirrung, M. C.; Plavoac, F.; White, C. T. In *Total Synthesis of Natural Products*; ApSimon, J., Ed.; John Wiley and Sons, Inc.: New York, 1983; Vol. 5, p 1. (c) Fischer, N. H.; Olivier, E. J.; Fischer, H. D. *Fortschr. Chem. Org. Naturst.* **1979**, *38*, 47.

(7) The stereochemical assignments of **4a–d** were based on NOE studies. Details are provided in the supplementary material.

(8) Wulff, W. D.; Challener, C. A.; Yang, D. C.; Faron, K. L.; Kim, O. K.; Xu, Y. C. Presented at the 197th National Meeting of the American Chemical Society, Dallas, TX, April 1989; paper ORGN 185.

(9) For recent discussions of the *gem*-dialkyl or Thorpe–Ingold effect, see: (a) Jung, M. E. *Synlett* **1990**, 186–190. (b) Jung, M. E.; Gervay, J. *J. Am. Chem. Soc.* **1991**, *113*, 224–232 and references cited therein.

(10) (a) For a discussion concerning the steric factors involved in divinylcyclopropane rearrangements, see: Piers, E.; Morton, H. E.; Nagakura, I.; Thies, R. W. *Can. J. Chem.* **1983**, *61*, 1226–1238 and citations therein. (b) Davies, H. M. L.; McAfee, M. J.; Oldenburg, C. E. M. *J. Org. Chem.* **1989**, *54*, 930. (c) For an example of a sterically inhibited *cis*-divinylcyclopropane rearrangement, see: Cantrell, W. R., Jr.; Davies, H. M. L. *J. Org. Chem.* **1991**, *56*, 723–727.

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).

$$\mathbf{12a} \xrightarrow[\text{benzene}]{60^{\circ}\text{C, 11 h}} \mathbf{10a}\ 70\% \qquad (2)$$

$$\mathbf{12b} \xrightarrow[\text{benzene}]{60^{\circ}\text{C, 7 h}} \mathbf{10b}\ 97\% \qquad (3)$$

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.

(2) For recent reviews, see: (a) Tomioka, K. *Synthesis* **1990**, 541. (b) Noyori, R. *Science* **1990**, *248*, 1194. (c) Taschner, M. J. In *Organic Synthesis: Theory and Application*; Hudlicky, T., Ed.; JAI Press: Greenwich, CT, 1989; Vol. 1, p 1.

(3) For recent reports, see: (a) Corey, E. J.; Imai, N.; Zhang, H.-Y. *J. Am. Chem. Soc.* **1991**, *113*, 728. (b) Narasaka, K.; Iwasawa, N.; Inoue, M.; Yamada, T.; Nakashima, M.; Sugimori, J. *J. Am. Chem. Soc.* **1989**, *111*, 5340 (asymmetric Diels–Alder reactions). (c) Evans, D. A.; Woerpel, K. A.; Hinman, M. M.; Faul, M. M. *J. Am. Chem. Soc.* **1991**, *113*, 726 (asymmetric cyclopropanations). (d) Mikami, K.; Terada, M.; Nakai, T. *J. Am. Chem. Soc.* **1990**, *112*, 3949 (asymmetric ene reactions). (e) Dieter, R. K.; Lagu, B.; Deo, N.; Dieter, J. W. *Tetrahedron Lett.* **1990**, 4105 (conjugate addition reactions). (f) Maruoka, K.; Banno, H.; Yamamoto, H. *J. Am. Chem. Soc.* **1990**, *112*, 7791 (asymmetric Claisen rearrangements). (g) Corey, E. J.; Kim, S. S. *J. Am. Chem. Soc.* **1990**, *112*, 4976 (aldol reactions). (h) Corey, E. J.; Yu, C.-M.; Lee, D.-H. *J. Am. Chem. Soc.* **1990**, *112*, 878. (i) Schmidt, B.; Seebach, D. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 99 (organometallic addition to aldehydes). (j) Soai, K.; Watanabe, M.; Yamamoto, A. *J. Org. Chem.* **1990**, *55*, 4832. (k) Hayashi, M.; Matsuka, T.; Oguni, N. *J. Chem. Soc., Chem. Commun.* **1990**, 1364. (l) Kaufmann, D.; Boese, R. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 545 and references cited in the above.

(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 ^1H 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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