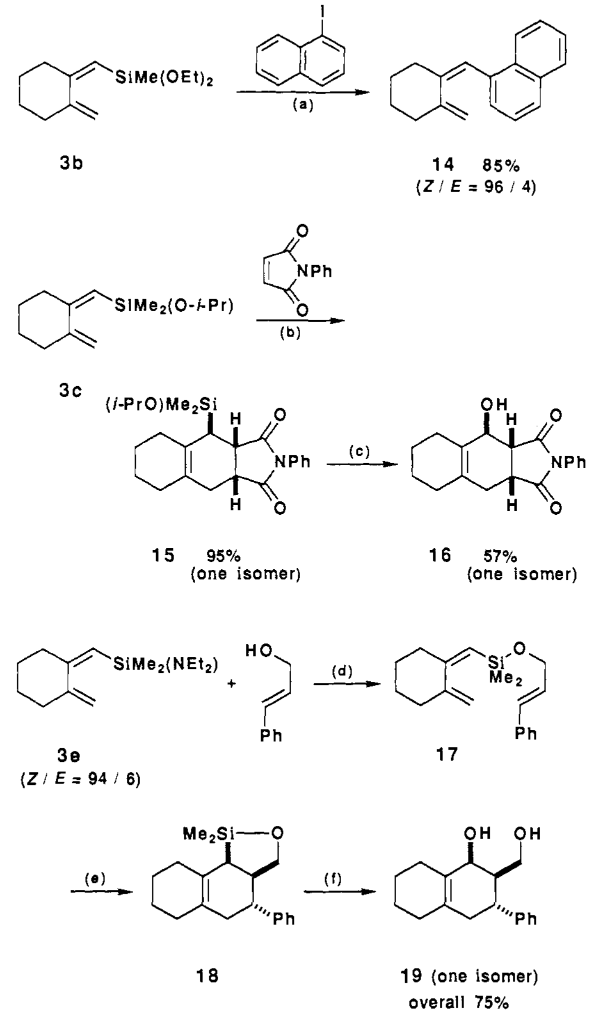
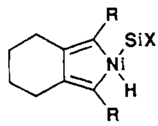
Scheme III[a]



[a] (a) $[PdCl(\eta^3\text{-}C_3H_5)]_2$ (2.5 mol %), $P(OEt)_3$ (5 mol %), TBAF (× 1.5), THF, 50 °C, 5 h. (b) Toluene, reflux, 14 h. (c) 30% H_2O_2 (× 3.6), KF (×2), $KHCO_3$ (×1), DMF, room temperature, 10 h. (d) Et_2O, room temperature, 10 h. (e) Xylene, reflux, 40 h. (f) 30% H_2O_2 (×3.6), KF (×2), $KHCO_3$ (×1), THF/MeOH, 50 °C, 18 h.

formed at all.[9,12] The stereoselectivity and regioselectivity observed in **12** are noteworthy in connection with the mechanism.

A stepwise mechanism shown in Scheme II seems to be plausible. Thus, the reaction may involve initial insertion of an acetylene into the Ni–Si bond rather than the Ni–H bond (step 2), subsequent insertion of the other acetylene into the resulting Ni–vinyl bond (step 3), and reductive elimination from the H–Ni–vinyl intermediate in the final step (4). The first insertion step is strongly supported by the regioselective introduction of the silyl group into the more reactive terminal acetylene observed in the unsymmetrical diyne **11**. Our previous work has demonstrated the insertion of acetylene into the Ni–Si bond to be the facile process.[13] Stereospecific cis insertion in both steps 2 and 3 is consistent with the observed stereochemistry. An alternative, traditional mechanism involving the initial insertion of terminal acetylene into the Ni–H bond[8,13d] may be ruled out, since no regioisomer **12′** was obtained from **11**. Another route involving a nickelacyclopentadiene intermediate **13** also seems to be less likely in view of the unfavorable Ni(IV) state. Details of the mechanism, including roles of phosphine ligands and aluminum species, will be clarified by further studies.



13

Exocyclic silyl dienes are useful synthetic intermediates, as exemplified by transformations of **3b**, **3c**, and **3e** (Scheme III). Thus, the C–Si bond in **3b** can be transformed to the C–C bond by palladium-catalyzed cross-coupling with an aryl iodide[14] to form **14**,[9] the *Z* configuration being highly retained. An intermolecular Diels–Alder reaction of **3c** gives **15**, which can be further transformed to polycyclic alcohol **16**[9] by hydrogen peroxide oxidation of the silicon–carbon bonds.[15] Furthermore, synthetic elaboration on the silicon of aminosilane **3e** makes possible the regio- and stereocontrolled intramolecular Diels–Alder reaction, as shown by transformation into **19** via **17** and **18**;[9] it should be noted that the exocyclic silyl diene is synthetically equivalent to an exocyclic dienol which exerts a regio- and stereocontrol ability. Other transformations of the promising *Z* exocyclic silyl dienes are now under investigation.

Acknowledgment. We thank H. Fujita for measurements of the 400-MHz NMR spectra and Dr. Seiki Saito, Okayama University, for valuable information on the preparation of optically active 1,7-diyne **4**.

Supplementary Material Available: A typical experimental procedure for preparation of **3** and spectral (^{1}H NMR, IR, ^{13}C NMR, and MS) and analytical data (elemental analysis) for compounds **3a–e**, **4**, **5**, **7**, **8**, **10**, **12**, **14**, **15**, **16**, and **19** (6 pages). Ordering information is given on any current masthead page.

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(12) In these cases, the starting diynes were completely consumed, the major product consisting of less volatile oligomers by intermolecular reaction.[8] 1,6-Heptadiyne and 1,8-nonadiyne gave only nonvolatile materials under similar condition.

(13) (a) Tamao, K.; Miyake, N.; Kiso, Y.; Kumada, M. *J. Am. Chem. Soc.* **1975**, *97*, 5603. (b) Kiso, Y.; Tamao, K.; Kumada, M. *J. Organomet. Chem.* **1974**, *76*, 95. (c) Kiso, Y.; Tamao, K.; Kumada, M. *J. Organomet. Chem.* **1974**, *76*, 105. (d) Kiso, Y.; Kumada, M.; Tamao, K.; Umeno, M. *J. Organomet. Chem.* **1973**, *50*, 297.

(14) (a) Hatanaka, Y.; Hiyama, T. *J. Org. Chem.* **1988**, *53*, 920; **1989**, *54*, 268. (b) Tamao, K.; Kobayashi, K.; Ito, Y. *Tetrahedron Lett.*, submitted for publication.

(15) E.g.: (a) Review: Tamao, K. *J. Synth. Org. Chem. Jpn.* **1988**, *46*, 861. (b) Tamao, K.; Maeda, K.; Yamaguchi, T.; Ito, Y. *J. Am. Chem. Soc.* **1989**, *111*, 4984, and our previous works cited therein.

Temperature Switching of Product Chirality upon Photosensitized Enantiodifferentiating Cis–Trans Isomerization of Cyclooctene

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Ever since the first report by Hammond and Cole in 1965,[1] the photosensitized enantiodifferentiating isomerizations in solution, though attempted with several sensitizers and substrates,[2-5] have never exceeded their original optical yield (7%)[1] for more than two decades. This is simply because the interaction between

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(1) Hammond, G. S.; Cole, R. S. *J. Am. Chem. Soc.* **1965**, *37*, 3256.

(2) Rau, H. *Chem. Rev.* **1983**, *83*, 535 and the references cited therein.

(3) Inoue, Y.; Kunitomi, Y.; Takamuku, S.; Sakurai, H. *J. Chem. Soc., Chem. Commun.* **1978**, 1024.

(4) Inoue, Y.; Takamuku, S.; Kunitomi, Y.; Sakurai, H. *J. Chem. Soc., Perkin Trans. 2* **1980**, 1672.

(5) Goto, S.; Takamuku, S.; Sakurai, H.; Inoue, Y.; Hakushi, T. *J. Chem. Soc., Perkin Trans. 2* **1980**, 1678.

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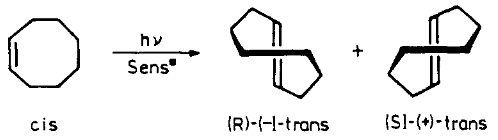
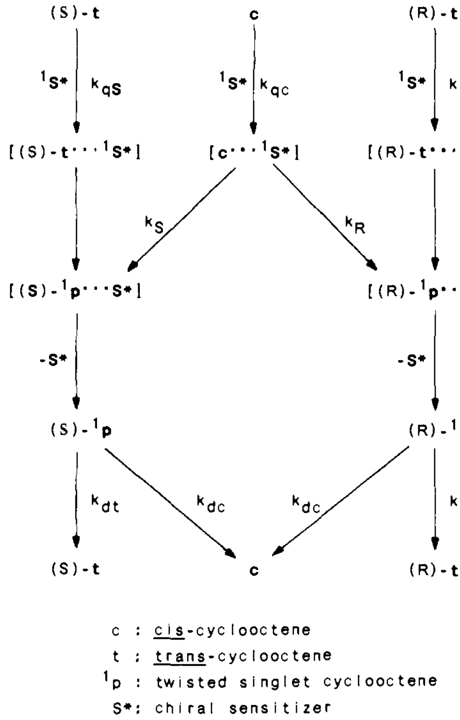
Scheme I



Scheme II



sensitizer and substrate is usually weak and short-lived in the excited state. Curiously, the temperature effect upon optical yield has never been examined with these photoreactions. In this communication we report a highly efficient photosensitized enantiodifferentiating cis–trans isomerization of cyclooctene, which gives high optical yields and shows unusual temperature effect upon optical yield.

In our earlier reports on the sensitized photoisomerization of simple alkenes via exciplex,[3-5] we have demonstrated briefly that the geometrical photoisomerization of *cis*-cyclooctene sensitized by chiral (−)-menthyl benzoate or isophthalate affords optically active (*R*)-(−)-*trans*-cyclooctene of 3–4% optical purity (op) at the early stages of reaction. Since the photoisomerization is obviously reversible, in the present study we first examined the effect of irradiation time, or conversion, upon optical yield in order to elucidate the stereodifferentiating step.[6] As shown in Table I, the optical yield obtained in the benzoate or terephthalate sensitization is practically invariant from the very initial stage to the photostationary state. This result indicates that the rotational relaxation rather than quenching process in Scheme II[4] is responsible for the photochemical enantiodifferentiation. This mechanism is further confirmed by the attempted photochemical kinetic resolution of racemic *trans*-cycloocene sensitized by (−)-menthyl benzoate, which merely resulted in a recovery of racemic trans (0.01–0.02% op) at low conversion (5–10%). It is concluded therefore that (*R*)- and (*S*)-trans isomers quench the excited singlet sensitizer (^{1}S*) at the same rate, i.e., $k_{qR} = k_{qS}$, whereas the rotational relaxation of the cis exciplex [c···^{1}S*] to the diastereomeric exciplexes proceeds at different rates, i.e., $k_R \neq k_S$.

Table I. Optical Yield of *trans*-Cyclooctene in the Sensitized Photoisomerization of Cis Isomer with Some Chiral Aromatic Esters[a]

sensitizer	% conv	$[\alpha]_D^{25}$	% op[b]
(−)-menthyl benzoate	2	−11.7	2.7
	4	−10.7	2.5
	11	−10.7	2.5
	21	−11.6	2.7
(−)-bornyl benzoate	18	−4.4	1.0
di-(−)-menthyl terephthalate	3	−25.6	6.0
	25	−25.4	6.0
di-(−)-menthyl isophthalate	24	−18.8	4.4
di-(−)-menthyl phthalate	9	+16.2	3.8
di-(−)-bornyl phthalate	9	+32.4	7.6
tetra-(−)-menthyl pyromellitate	9	−39.9	9.4
tetra-(−)-bornyl pyromellitate	6	−49.1	11.5

[a] For experimental details, see ref 4 and 6. [b] Optical purity based on the reported $[\alpha]_D^{25}$ value of −426° (*c* 0.41, CH_2Cl_2) for (*R*)-(−)-*trans*-cyclooctene: Cope, A. C.; Canellin, C. R. *J. Am. Chem. Soc.* **1963**, *85*, 3276.

The structural and electronic effects of chiral alcohol moiety and nuclear substitution in aromatic ester were surveyed to some extent (Table I). The introduction of additional chiral alkoxycarbonyl group(s) to benzoate enhances the optical yield substantially. (−)-Menthyl or (−)-bornyl esters of terephthalic, isophthalic, and pyromellitic acid gave the (*R*)-(−)-trans in greater optical yields by factors of 2–10 than the parent benzoate. Bornyl pyromellitate recorded the highest optical yield of 11.5% as a photosensitized enantiodifferentiating reaction at room temperature. Quite interestingly, (−)-menthyl and (−)-bornyl phthalates afforded the antipode, (*S*)-(+)-trans, in spite of the same configuration of alcohol moiety in the sensitizer.

Unusual behavior of ortho dicarboxylate sensitizers was also observed in the temperature-dependence study. Using (−)-menthyl and/or (−)-bornyl esters of benzoic, phthalic, terephthalic, and pyromellitic acid as chiral sensitizers, the photosensitizations were performed at a variety of temperatures ranging from −88 to +50 °C. In Figure 1, logarithm of relative rate constant k_S/k_R, or ln [(100 + % op)/(100 − % op)],[7] is plotted as a function of reciprocal temperature. In the menthyl benzoate and terephthalate sensitizations, the optical yield decreases with increasing temperature affording a good straight line. As expected the extrapolation of the line gives virtually zero optical yield at the infinite temperature.

By contrast, the phthalate and pyromellitate sensitizations led to quite different results. They also give good straight lines, which however go across the zero percent op line at finite temperatures as shown in Figure 1. Indeed, the direction of product's optical rotation is inverted at −19 °C in the menthyl pyromellitate sensitization. With the other phthalates and pyromellitate, a similar phenomenon is predicted at higher temperatures (90–125 °C). Below this critical temperature, designated tentatively as isoenantiodifferentiating temperature T_0, the pyromellitate photosensitization affords predominantly the (*S*)-(+)-trans and the optical yield increases with decreasing temperature to give the highest optical yield of 40.6% at −88 °C with (−)-bornyl pyromellitate. Extrapolation of these results, assuming continued linear relationship at low temperature, leads to a prediction of essentially complete stereochemical control at −245 °C. Above T_0, the antipode with the (*R*) configuration is the major photoproduct, and *its optical yield increases as the irradiation temperature increases*, approaching the ultimate optical yields of 12–63% at infinite temperature.

This unexpected temperature dependence of optical yield may be accounted for by postulating two diastereomeric conformers for the excited aromatic ortho dicarboxylate, the population of which varies with the temperature. It is inferred that one excited-state conformer, which gives (*S*)-(+)-trans, is the predom-

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(6) A pentane solution (300 mL) of *cis*-cyclooctene (0.2 M) and a chiral sensitizer (5–10 mM) in an annular quartz vessel, surrounding a 30-W mercury resonance lamp (Vycor filter), was irradiated under an argon atmosphere in a thermostated bath (±1 °C) for a period indicated, mostly enough to establish the photostationary state. The photolysate was extracted at 0 °C with aqueous silver nitrate to isolate the trans isomer according to similar procedures described previously.[4] The optical rotations were measured on a Jasco DIP-360 and/or a Perkin-Elmer 243B polarimeter.

(7) In this calculation, the optical purity (% op) possesses the same sign as the optical rotation.

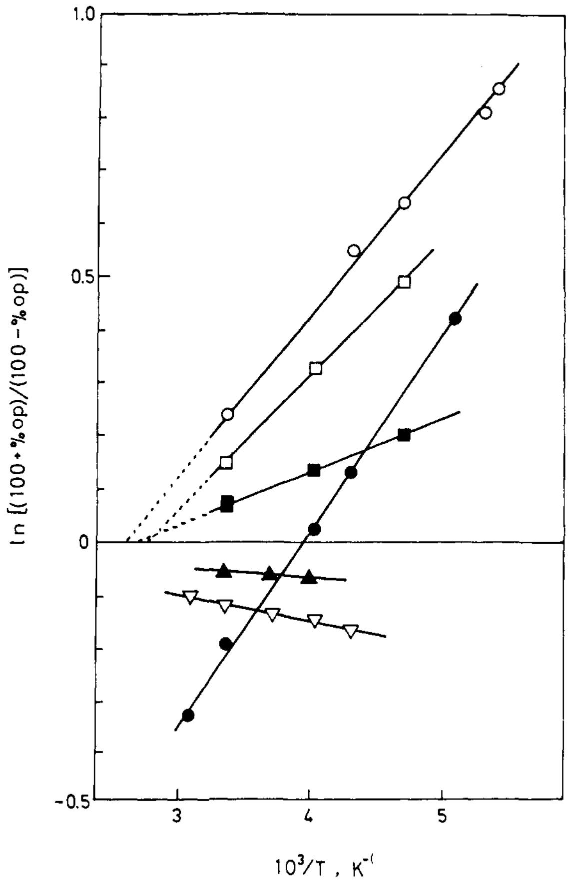

Figure 1. Plot of ln [(100 + % op)/(100 − % op)] as a functin of reciprocal temperature in the enantiodifferentiating photoisomerization of *cis*-cyclooctene sensitized by (−)-menthyl benzoate (▲), di-(−)-menthyl terephthalate (▽), di-(−)-menthyl (■) and di-(−)-bornyl phthalate (□), and tetra-(−)-menthyl (●) and tetra-(−)-bornyl pyromellitate (○) in pentane solution.

inant species at low temperatures, while another prevails at high temperatures to give (*R*)-(−)-trans. Although the precise structures of the diastereomeric excited states, each of which gives the antipode, are not necessarily easy to depict at present, the fact that only ortho dicarboxylates exhibit the unusual temperature dependence may indicate the presence of some steric hindrance between adjacent bulky chiral alcohol moieties.

Further study to obtain insights into the nature of excited aromatic esters and the kinetics of photosensitization is currently in progress along with the search for more effective chiral photosensitizers.

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Asymmetric Induction in a Palladium-Catalyzed TMM Cycloaddition. Mechanistic Implications Regarding the Reactive Intermediate

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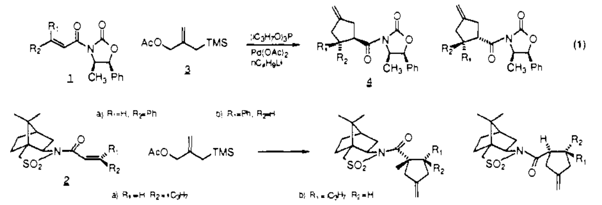
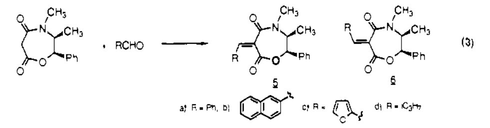
Received April 10, 1989

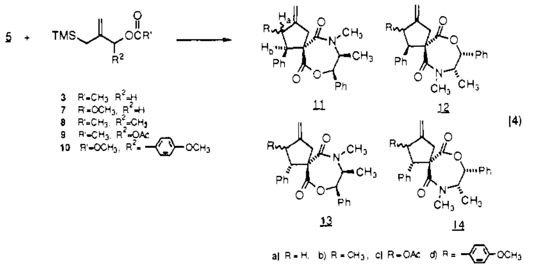
In conjunction with the application of palladium-catalyzed cycloadditions of 2-((trimethylsilyl)methyl)-3-acetoxy-1-propene and its derivatives, the prospects for asymmetric induction become important.[1,2] The establishment that the bond-making process occurs on the face of the TMM unit distal to palladium makes asymmetric induction by use of chiral phosphine ligands somewhat remote.[3] Use of chiral auxiliaries of the type utilized in many Lewis acid catalyzed Diels–Alder reactions (cf. eq 1[4] and eq 2[5]) also does not necessarily extend to this cycloaddition. With oxazolidin-2-ones **1**, diastereofacial selectivity amounted to 20–26% (**4a** major cycloadduct by X-ray crystallography) and, with camphorsultams **2**, to 4–26%. In both cases, the *Z* acceptors **1b** and **2b** exhibit the higher selectivity. These results stand in contrast to the Ni-catalyzed co-oligomerization with such chiral acceptors where good diastereoselectivity is observed.[6]



Attributing the lack of adequate diastereofacial selectivity to the conformational mobility of the acceptors in the absence of Lewis acids, which are typically employed in the Diels–Alder reactions, we turned to an acceptor which would be inherently conformationally more rigid, **5** or **6**. The latter is readily prepared by Knoevenagel condensation (eq 3), which gives the *Z* isomer **5** in all of our cases except furfural, which gives the *E* isomer **6c** preferentially.[7,8]



Cycloaddition of **5a** with the TMM precursor **3** using a catalyst derived from 2.5 mol% of $(dba)_3Pd_2 \cdot CHCl_3$ and 10 mol% of dppf



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† In part.

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(2) For reactions of methylenecyclopropenes in cycloaddition, see: Binger, P.; Buch, M. *Top. Curr. Chem.* **1987**, *135*, 77.

(3) Trost, B. M.; Nanninga, T. N. *J. Am. Chem. Soc.* **1985**, *107*, 1075. For modest ee in a related cycloaddition, see: Yamamoto, A.; Ito, Y.; Hayashi, T. *Tetrahedron Lett.* **1989**, *30*, 375.

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(6) Binger, P.; Schafer, B. *Tetrahedron Lett.* **1988**, *29*, 529. Also, see: Binger, P.; Brinkmann, A.; Richter, W. J. *Tetrahedron Lett.* **1983**, *24*, 3599.

(7) This model was originally put forth by Tietze for the intramolecular Diels–Alder reaction, see: Tietze, L. F.; Brand, S.; Pfeiffer, T.; Antel, J.; Harms, K.; Sheldrick, G. M. *J. Am. Chem. Soc.* **1987**, *109*, 921.

(8) Mukaiyama, T.; Takida, T.; Fujimoto, K. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 3368. Hirako, Y.; Mukaiyama, T.; Takeda, T. *Chem. Lett.* **1978**, 461. Fujimoto, K.; Mukaiyama, T.; Takeda, T. *Chem. Lett.* **1978**, 3368; **1979**, 1207. Hoshiko, T.; Mukaiyama, T.; Takeda, T. *Chem. Lett.* **1981**, 797. Also, see: Brown, R. T.; Ford, M. J. *Synth. Commun.* **1988**, *18*, 1801. There is question regarding the assignment of the geometry of the acceptors utilized in the cuprate addition. A re-examination of this question may lead to a stereochemical assignment consistent with the results of Tietze and ours.

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