Scheme I

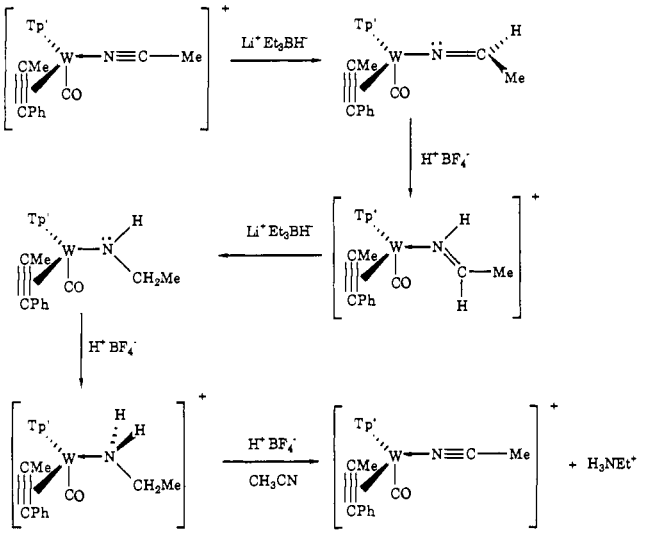

Table I. Selected Data for Intermediates in the Reduction of Coordinated Acetonitrile

complex	color	ν_{CO}, cm^{-1}	alkyne ^{13}C, ppm
$[Tp'(CO)(PhC_2Me)W{\leftarrow}N{\equiv}CCH_3][BF_4]$	blue	1940	215, 213
$Tp'(CO)(PhC_2Me)W{-}N{=}CHCH_3$	orange	1885	160, 159
$[Tp'(CO)(PhC_2Me)W{\leftarrow}NH{=}CHCH_3][BF_4]$	blue	1920	215, 214
$Tp'(CO)(PhC_2Me)W{-}NHCH_2CH_3$	orange	1854	169, 167
$[Tp'(CO)(PhC_2Me)W{\leftarrow}NH_2CH_2CH_3][BF_4]$	blue	1909	215, 213

properties constitutes about 20% of the product.

Protonation at the azavinylidene nitrogen in CH_2Cl_2 solution generates a blue cationic imine complex, $[Tp'(CO)(PhC{\equiv}CMe)W(NH{=}CHMe)][BF_4]$ (90% yield). The ^{13}C NMR spectrum indicates that formation of the imine has returned the alkyne to a four-electron-donor role (alkyne carbons: 215, 214 ppm). Coupling information from ^1H NMR is informative (10.86 ppm, 1 H, broad d, $^3J_{HH}$ = 20 Hz, N*H*; 6.38 ppm, 1 H, dq, $^3J_{HH}$ = 20 Hz, 6 Hz, NH=C*H*CH_3; 2.22 ppm, dd, 3 H, $^3J_{HH}$ = 6 Hz, $^4J_{HH}$ = 1 Hz, NH=CHC*H*$_3$).

The coordinated imine is activated for further reduction. Hydride addition at carbon with $Li[HBEt_3]$ in THF forms an ethylamido ligand in the neutral orange $Tp'(CO)(PhC{\equiv}CMe)W{-}NHCH_2CH_3$ product (75% yield). Again the nitrogen lone pair competes with the alkyne $\pi_\perp$ orbital for donation into the lone vacant metal d_π orbital (alkyne carbons at 169 and 167 ppm). The methylene protons of the amidoethyl group are diastereotopic since the metal is chiral, and assignment of the ^1H NMR is straightforward. As in the neutral azavinylidene product, two isomers are evident in the ^1H and ^{13}C NMR in a 4:1 ratio. We believe these isomers result from restricted rotation about the metal-nitrogen bond.

Protonation of the neutral amido complex in 1:5 CH_2Cl_2/Et_2O completes reduction of the nitrile as the blue cationic ethylamine complex forms. The ^1H NMR properties of the ethylamine ligand are very similar to those of the ethylamine ligand in $[(triars)HRu(NH_2CH_2CH_3)]^+$.[3] The amine ligand can be removed as the ethylammonium salt by addition of excess acid to the amine complex in acetonitrile to regenerate the starting acetonitrile adduct.

We have no mechanistic information. Nucleophilic attack on four-electron-donor alkyne ligands is known to form η^2-vinyl products in other d^4 monomers.[8] Indeed we have isolated η^2-vinyl products from hydride addition to $[Tp'(CO)_2W(PhC{\equiv}CH)][BF_4]$,[9] so initial attack at the alkyne is a possibility in the acetonitrile reduction reactions. Nitrile insertion into metal-alkyl bonds has been reported,[10] and we cannot rule out initial nucleophilic attack at the metal by the hydride reagent. Given the steric bulk of the Tp' ligand, which is known to inhibit metal-based reactions in related systems,[11] we favor direct attack at the acetonitrile carbon by $Li[HBEt_3]$. Protonation at the nitrogen lone pair also seems more attractive than metal protonation followed by hydrogen migration to the α-nitrogen position.

Regardless of the mechanism, this system illustrates one sequence of reactions that converts metal-bound nitriles to amines. The stepwise reduction of the acetylide triple bond in $Fp'{-}C{\equiv}CH$ to form $Fp'{-}CH_2CMe_3$ capitalized on the nucleophilicity of C_α and the electrophilicity of C_β in unsaturated η^1 carbon ligands.[12] Such reactions reflect the ability of the metal to house lone pairs or form π bonds while adhering to the 18-electron rule.[13] The reactivity pattern in the acetonitrile reduction is reversed, as expected, since it is the nitrogen that alternates between accommodating a lone pair and forming a covalent bond. No doubt the flexible electron-donor capability of the alkyne $\pi_\perp$ orbital in this system is important in accounting for the stability of these nitrile reduction intermediates.

Acknowledgment. We are grateful to the National Science Foundation for support of this work.

Supplementary Material Available: Experimental procedures, complete ^1H and ^{13}C NMR data, and elemental analyses for $Tp'(CO)(PhC_2Me)WI$ and **1-5** (5 pages). Ordering information is given on any current masthead page.

(8) (a) Allen, S. R.; Beevor, R. G.; Green, M.; Norman, N. C.; Orpen, A. G.; Williams, I. D. *J. Chem. Soc., Dalton Trans.* **1985**, 435. (b) Davidson, J. L.; Wilson, W. F.; Manojlovic-Muir, L.; Muir, K. *J. Organomet. Chem.* **1983**, *254*, C6. (c) Morrow, J. R.; Tonker, T. L.; Templeton, J. L. *J. Am. Chem. Soc.* **1985**, *107*, 6956.

(9) Feng, S. G.; Templeton, J. L., unpublished results.

(10) (a) Bercaw, J. E.; Davies, D. L.; Wolczanski, P. T. *Organometallics* **1986**, *5*, 443. (b) Bochmann, M.; Wilson, L. M.; Hursthouse, M. B.; Motevalli, M. *Organometallics* **1988**, *7*, 1148. (c) Simpson, S. J.; Andersen, R. A. *J. Am. Chem. Soc.* **1981**, *103*, 4063. (d) Jordan, R. F.; Bajgur, C. S.; Dasher, W. E. *Organometallics* **1987**, *6*, 1041.

(11) (a) Bruce, A. E.; Gamble, A. S.; Tonker, T. L.; Templeton, J. L. *Organometallics* **1987**, *6*, 1350. (b) Desmond, T.; Lalor, F. J.; Ferguson, G.; Ruhl, B. *J. Chem. Soc., Chem. Commun.* **1983**, 55.

(12) Davison, A.; Selegue, J. P. *J. Am. Chem. Soc.* **1980**, *102*, 2455.

(13) Birdwhistell, K. R.; Tonker, T. L.; Templeton, J. L. *J. Am. Chem. Soc.* **1985**, *107*, 4474.

Nickel(0)-Catalyzed Cyclization of 1,7-Diynes via Hydrosilation: One-Step Synthesis of 1,2-Dialkylidenecyclohexanes with a (*Z*)-Vinylsilane Moiety

Kohei Tamao,* Kenji Kobayashi, and Yoshihiko Ito*

Department of Synthetic Chemistry, Faculty of Engineering Kyoto University, Kyoto 606, Japan

Received December 27, 1988

1,2-Dialkylidenecycloalkanes are useful building blocks for the synthesis of polycyclic molecules.[1] Three methodologies have recently been developed: (1) Cyclization of 1,*n*-diynes with stoichiometric amounts of titanium or zirconium complexes[2] or with palladium catalysts,[3] (2) palladium[4] or nickel-chromium-

(1) E.g.: (a) Schore, N. E. *Chem. Rev.* **1988**, *88*, 1081. (b) Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 539.

(2) (a) Nugent, W. A.; Thorn, D. L.; Harlow, R. L. *J. Am. Chem. Soc.* **1987**, *109*, 2788. (b) Negishi, E.; Holmes, S. J.; Tour, J. M.; Miller, J. A.; Cederbaum, F. E.; Swamspm, D. R.; Takahashi, T. *J. Am. Chem. Soc.* **1989**, *111*, 3336.

(3) Trost, B. M.; Lee, D. C. *J. Am. Chem. Soc.* **1988**, *110*, 7255. In their reaction, hydrosilanes act as reductants instead of hydrosilation agents. Palladium-catalyzed cyclization of a 1,6-diyne with Me_3SiCN has also been reported to give exocyclic silyl diene derivatives in low yields. Chatani, N.; Takeyasu, T.; Horiuchi, N.; Hanafusa, T. *J. Org. Chem.* **1988**, *53*, 3539.

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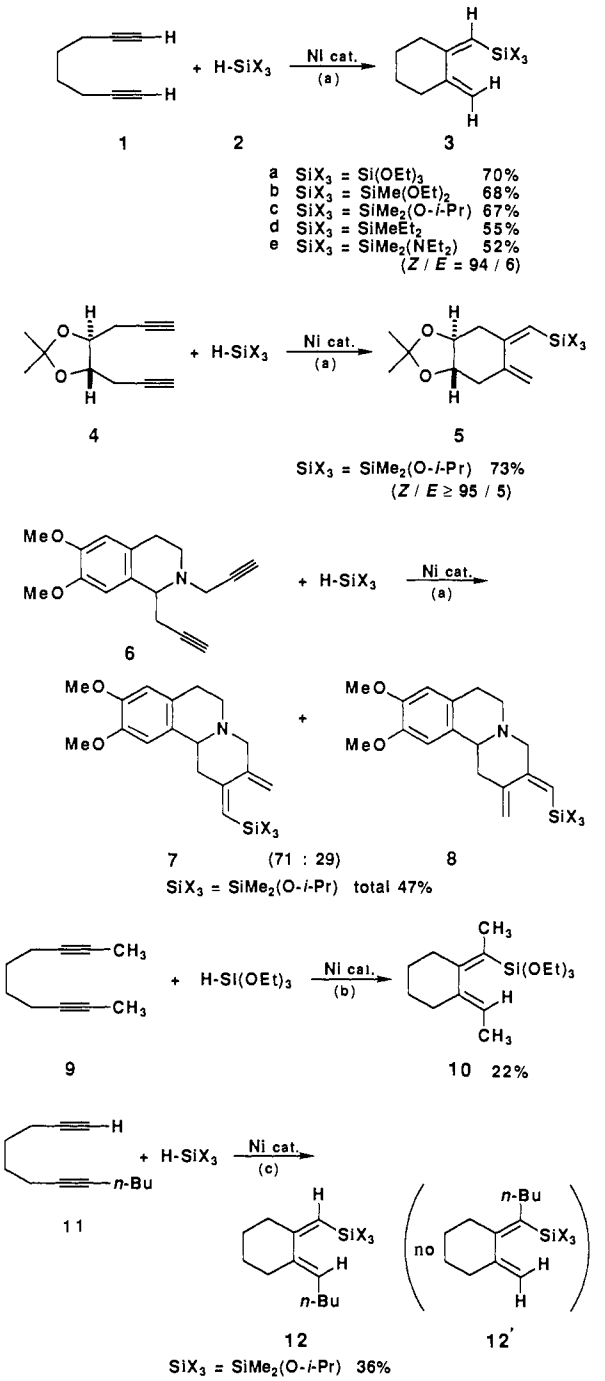
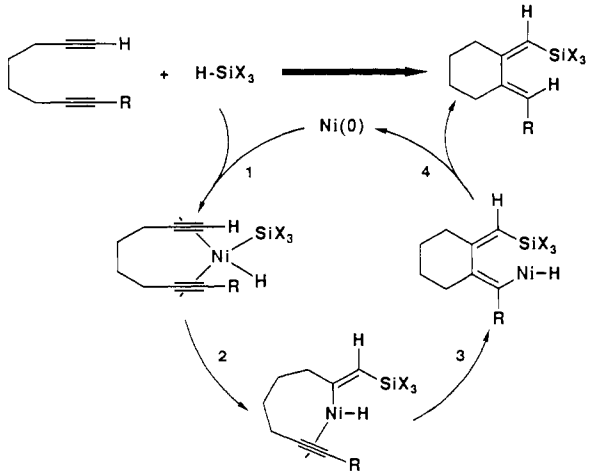
Scheme I[a]



[a](a) $Ni(acac)_2$ (1 mol %), DIBAH (2 mol %), benzene (0.5 M solution), 50 °C, 6 h. (b) $Ni(acac)_2$ (1 mol %), DIBAH (2 mol %), PPh_3 (2 mol %), toluene (0.5 M solution), 100 °C, 12 h. (c) $Ni(acac)_2$ (1 mol %), DIBAH (2 mol %), benzene (0.05 M solution), 50 °C, 24 h.

catalyzed[5] cyclization of 1,*n*-enynes, and (3) 1,4-elimination of allylsilane-based precursors.[6] It should be mentioned here that these methods provide (*E*)- or (*E*,*E*)-diene skeletons only (no *Z* substituent available).[7]

Scheme II[a]



[a]Other ligands on nickel are omitted for clarity.

Reported herein is a new cyclization of 1,7-diynes via nickel(0)-catalyzed hydrosilation to 1,2-dialkylidenecyclohexanes with a (*Z*)-vinylsilane moiety (hereafter, abbreviated to exocyclic silyl dienes). Representative results are shown in Scheme I.[8]

Reactions of 1,7-octadiyne (**1**) with mono-, di-, and trialkoxysilanes, monoaminosilanes, and trialkylsilanes **2** all gave *Z* exocyclic silyl dienes **3** in stereochemically pure states except **3e** in $Z/E = 94/6$.[9,10]

The cyclization has been applied to an optically active 1,7-octadiyne derivative **4**[11] to give an optically active exocyclic silyl diene **5** in high yield;[9] since **4** has a C_2 symmetry axis, the introduction of the silyl group into either acetylene bond forms the same optically active product.

A nitrogen-containing, unsymmetrical 1,7-octadiyne derivative **6** reacted similarly to form a regioisomeric mixture of alkaloid-like tricyclic silyl dienes **7** and **8** in a ratio of 71/29;[9] the regioselectivity is not very high, but suggests an interesting directing effect by the nitrogen atom.

Internal acetylene **9** was less reactive and reacted only under more severe conditions in the presence of triphenylphosphine as an accelerating additive to give **10** in low yields, but as a single stereoisomer.[9] Unsymmetrical diyne **11**, which contains both terminal and internal acetylenes, reacted under the mild standard condition to form **12** in which the silyl group is introduced into the terminal acetylene carbon exclusively, no regioisomer **12'** being

(4) (a) Trost, B. M.; Lautens, M. *J. Am. Chem. Soc.* **1985**, *107*, 1781. (b) Trost, B. M.; Chung, J. Y. L. *J. Am. Chem. Soc.* **1985**, *107*, 4586. (c) Trost, B. M.; Chen, S.-F. *J. Am. Chem. Soc.* **1986**, *108*, 6053. (d) Trost, B. M.; MacPherson, D. T. *J. Am. Chem. Soc.* **1987**, *109*, 3483.

(5) Trost, B. M.; Tour, J. M. *J. Am. Chem. Soc.* **1987**, *109*, 5268.

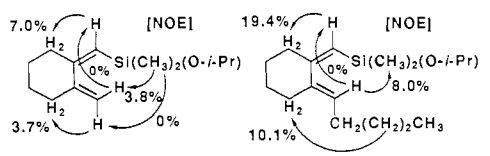
(6) (a) Trost, B. M.; Shimizu, M. *J. Am. Chem. Soc.* **1982**, *104*, 4299; **1983**, *105*, 6757. (b) Hosomi, A.; Otaka, K.; Sakurai, H. *Tetrahedron Lett.* **1986**, *27*, 2881. (c) Hosomi, A.; Hoashi, K.; Kohra, S.; Tominaga, Y.; Otaka, K.; Sakurai, H. *J. Chem. Soc., Chem. Commun.* **1987**, 570. (d) Hatanaka, Y.; Kuwajima, I. *J. Org. Chem.* **1986**, *51*, 1932.

(7) This is the case also in *o*-quinodimethanes: Ito, Y. In *Current Trends in Organic Synthesis*; Nozaki, H., Ed.; Pergamon: Oxford, 1983; pp 169–175.

(8) This is an intramolecular version of excellent work originally reported by Lappert and co-workers: Lappert, M. F.; Nile, T. A.; Takahashi, S. *J. Organomet. Chem.* **1974**, *72*, 425. They obtained a mixture of head-to-head and head-to-tail dimerization–hydrosilation products from terminal acetylenes, favored (*E*)-vinylsilane skeletons, and observed no reaction with internal acetylenes. In contrast, our present intramolecular reaction has shown entirely different results in all respects.

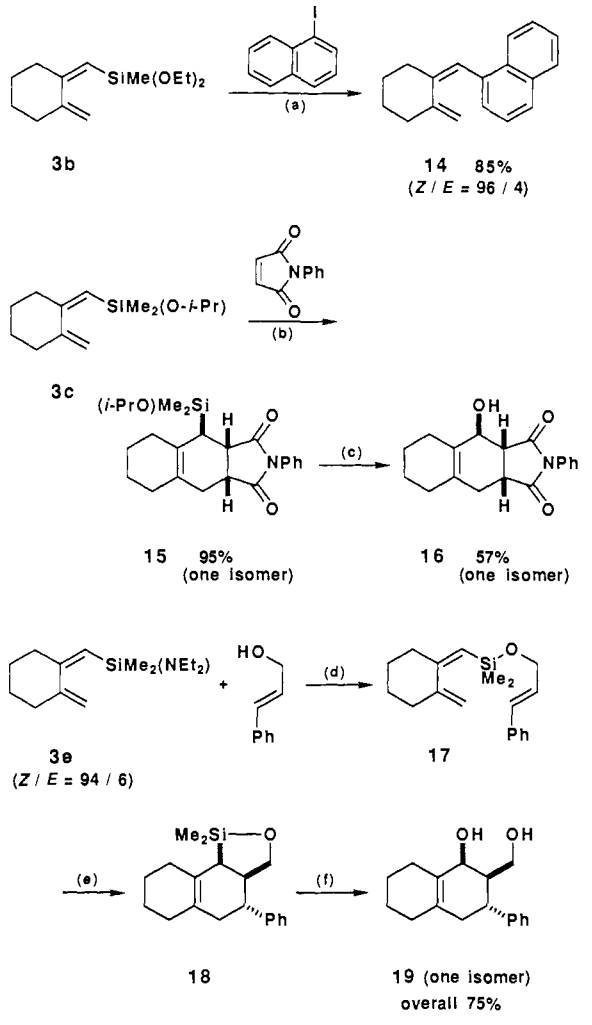
(9) All new compounds showed satisfactory spectral and analytical data (see Supplementary Material).

(10) The stereochemistry of the diene part was deduced by NOE analysis, as exemplified by the following data.



(11) Diyne **4** was prepared from optically active (*S*,*S*)-1,2:3,4-diepoxybutane [Seebach, D.; Kalinowski, H.-O.; Bastani, B.; Crass, G.; Daum, H.; Dorr, H.; DuPreez, N. P.; Ehrig, V.; Langer, W.; Nussler, C.; oei, H.-A.; Schmitt, M. *Helv. Chim. Acta* **1977**, *60*, 301] by a sequence of silylethynylation ($Me_3SiC{\equiv}CLi$, $BF_3{\cdot}OEt_2$, THF), acetonization ($Me_2C(OMe)_2$, TsOH), and desilylation (NaOH, $PhCH_2NEt_3Cl$, MeCN, H_2O) in 73% overall yield. Cf.: Hatakeyama, S.; Sakurai, K.; Saijo, K.; Takano, S. *Tetrahedron Lett.* **1985**, *26*, 1333.

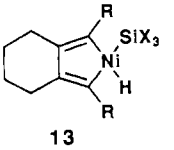
Scheme III[a]



[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 (^1H 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.

(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

Yoshihisa Inoue,* Taizo Yokoyama, Noritsugu Yamasaki, and Akira Tai

Basic Research Laboratory
Himeji Institute of Technology
2167 Shosha, Himeji, Hyogo 671-22, Japan

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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

(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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