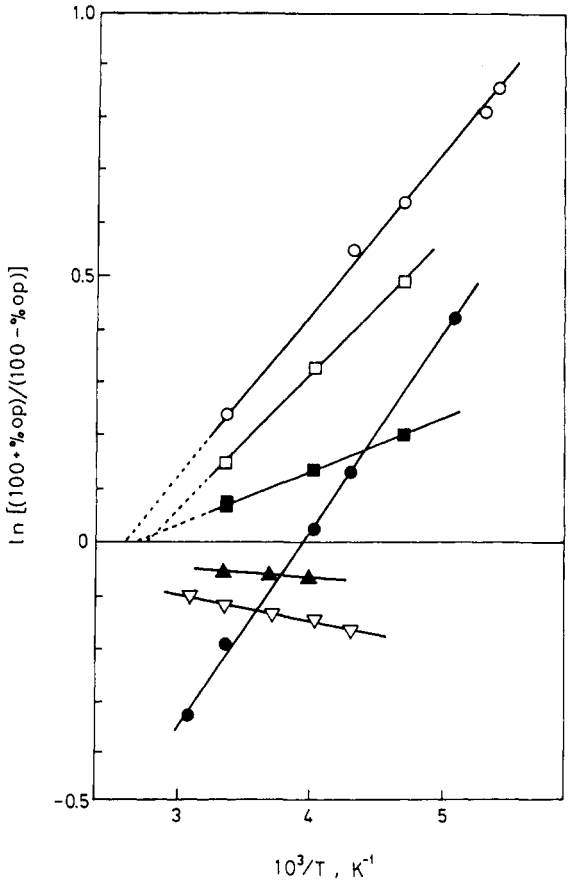

Figure 1. Plot of ln [(100 + % op)/(100 - % op)] as a functin of reciprocal temperature in the enantiodifferentiating photoisomerization of *cis*-cyclooctene sensitized by (-)-menthyl benzoate (▲), di-(-)-menthyl terephthalate (▽), di-(-)-menthyl (■) and di-(-)-bornyl phthalate (□), and tetra-(-)-menthyl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

Acknowledgment. This work was supported in part by a Grant-in-Aid for Scientific Research (No. 63550630) from the Ministry of Science, Culture and Education of Japan, which is gratefully acknowledged.

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

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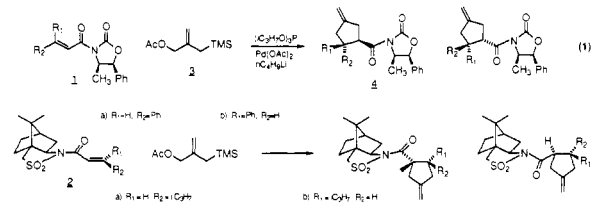
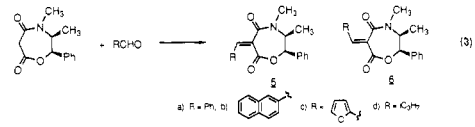
In conjunction with the application of palladium-catalyzed cycloadditions of 2-((trimethylsilyl)methyl)-3-acetoxy-1-propene and its derivatives, the prospects for asymmetric induction become important.[1,2] The establishment that the bond-making process occurs on the face of the TMM unit distal to palladium 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])

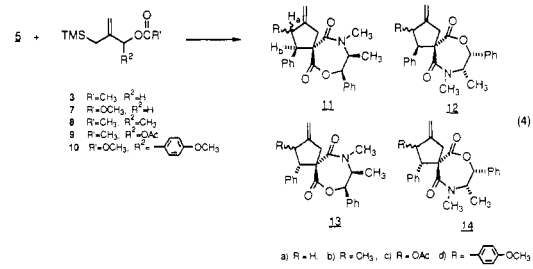


also does not necessarily extend to this cycloaddition. With oxazolidin-2-ones **1**, diastereofacial selectivity amounted to 20-26% (**4a** major cycloadduct by X-ray crystallography) and, with camphorsultams **2**, to 4-26%. In both cases, the *Z* acceptors **1b** and **2b** exhibit the higher selectivity. 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



† In part.

(1) Trost, B. M. *Angew Chem., Int. Ed. Engl.* **1986**, *25*, 1.
(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.
(4) Evans, D. A.; Chapman, K. T.; Bisaha, J. *J. Am. Chem. Soc.* **1988**, *110*, 1238.
(5) Oppolzer, W.; Rodriguez, I.; Blagg, J.; Bernardinelli, G. *Helv. Chim. Acta* **1989**, *72*, 123. For diastereoselective 1,3-dipolar cycloadditions, see: Curran, D. P.; Kim, B. H.; Daugherty, J.; Heffner, T. A. *Tetrahedron Lett.* **1988**, *29*, 3555.
(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.
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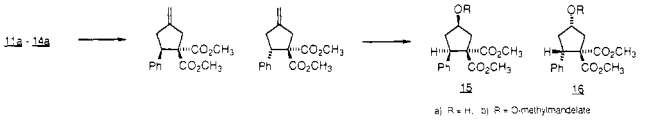
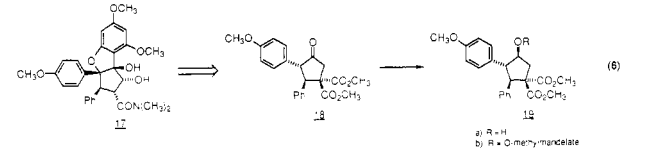
in THF at 70 °C gives a 75:25 mixture of two adducts (88%), whereas a 23:79 ratio is obtained in 1:1 toluene/dioxane at 110 °C using **7**, triisopropylphosphite, palladium acetate, and *n*-butyllithium to generate the active catalyst (>70% yield). In order to assess which of the four possible adducts **11a–14a** form and to show the utility of these adducts, we converted the oxazepandione (NaOH, C_2H_5OH, 80 °C; acidify with 2N HCl; ether, CH_2N_2, 88–90% yield) to the dimethyl ester with recovery of the chiral auxiliary (eq 5). Reductive ozonolysis (O_3, CH_3OH, −78



(5)

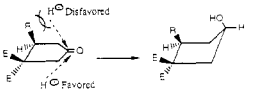
°C then add $NaBH_4$, 76% yield) gives the enantiomeric cyclopentanols *as single diastereomers*. To demonstrate the *Z* relative stereochemistry, Eu(fod)$_3$ induced shifts of the *Z* alcohols **15a** and **16a** and the corresponding *E* alcohols obtained by the Mitsunobu procedure (Ph_3P, DEADCAT, HOAc; K_2CO_3, H_2O; CH_2N_2; 65%) in which the benzylic proton in **15a** and **16a** shifts half as fast ($\Delta\delta$ 0.068) as the same proton in the *E* isomer ($\Delta\delta$ 0.146) indicates this proton is trans to the hydroxyl group (i.e., phenyl and hydroxyl groups cis) in **15a** and **16a**. Conversion of the alcohols **15a** and **16a** to the *O*-methylmandelates **15b** and **16b** reveals the alcohol is >97% enantiomerically pure and possesses the (1*R*,4*R*) configuration (**15a**).[9] Thus, the cycloaddition provides a mixture of cycloadducts **11a** and **12a** which indicates excellent diastereofacial selectivity (>97%) but a variation of geometrical selectivity. This result firmly establishes that the scrambling of geometry in the reaction does not arise from loss of the olefin geometry of the starting material.[10] Interconversion of olefin isomers of the starting material must lead to isomers epimeric at the carbon bearing the phenyl group which is not observed experimentally.

Only the cycloadditions using the parent TMM donors **3** or **7** show this geometrical scrambling. Our desire to employ this reaction for an asymmetric synthesis of the antileukemic rocaglamide **17**[11] led to use of the *p*-anisyl substituted donor **10**. By



(6)

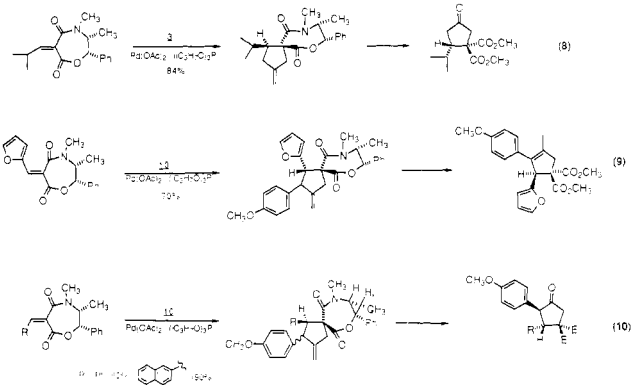
using a catalyst prepared in situ from palladium acetate and triisopropylphosphite, with or without *n*-butyllithium, provides a 76–90% yield of a cycloadduct as a mixture (up to 4:1) of two diastereomers. That 2,3-ring geometry and not facial selectivity accounts for the mixture derived from ozonolysis, which produces a single cyclopentanone. Facile equilibration of the cyclopentanone to the thermodynamically more stable trans-2,3-disubstituted system establishes the diastereofacial selectivity of attack of the TMM on the acceptor to be complete (>98%). Establishment of the stereochemistry as depicted in **11d** derives from removal of the chiral auxiliary (vide supra) and ozonolysis [O_3, CH_3OH, −78 °C then $(CH_3)_2S$] to the single ketone **18**. Diastereoselective reduction ($NaBH_4$, CH_3OH, 0 °C) is completely controlled by the 3-aryl rather than the 2-aryl substituent to give the alcohol **19a**. Confirmation of this stereochemistry derives from a Eu(3+) induced shift study of this alcohol and its epimer prepared by the Mitsunobu procedure as delineated for the related alcohols **15a** and **16a**. The complete control of the diastereoselectivity of reduction of the cyclopentanone by the more distant substituent appears general and is in accord with a trajectory of hydride attack corresponding to the Dunitz–Burgi angle[12] as depicted in eq 7.



(7)

The methyl and acetoxy substituted donors **8** and **9** give analogous results, whereas the cycloadducts, obtained in 80% and 58% yields, respectively, arise by attack with >93% facial selectivity. By analogy to the above cases, we assign the stereochemistry as depicted in **11b** and **11c**.

The ready variability of the substituent of the acceptor according to eq 3 translates this diastereoselective cycloaddition into an excellent general enantiocontrolled cyclopentane synthesis as outlined in eq 8–10. Either enantiomeric series is available either



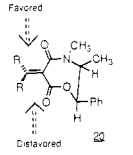
(8)

(9)

(10)

by changing olefin geometry (eq 9) or by using the enantiomeric chiral auxiliary (eq 8 and 10). *In all cases of the Z acceptor, the facial selectivity with respect to the acceptor was >96%!* For the *E* acceptor, the facial selectivity dipped to 90%. As an alternative to oxidative cleavage of the exocyclic methylene group, double bond isomerization (eq 9, $RhCl_3 \cdot 3H_2O$, C_2H_5OH, H_2O, 80 °C, 67%)[13] converts this cycloaddition into an enantiocontrolled cyclopentene annulation.

The stereochemistry of the cycloadducts corresponds to attack syn to the phenyl and methyl substituents of the chiral auxiliary! This result is in accord with the acceptor reacting through the conformer depicted in **20** where the substituents bow the acceptor to create concave and convex surfaces such that the reagent attacks the convex face.[7,8]



This asymmetric construction of cyclopentyl derivatives is richly diverse. As demonstrated, various substituted trimethylenemethanes and various substituted acceptors allow quite a wide selection of ring substituents. The exocyclic methylene group can be utilized directly (i.e., reduction to a methyl group, Markovnikov hydration to a methylcarbinol, or anti-Markovnikov hydration to a hydroxymethyl group, etc.), cleaved to a cyclopentanone, cleaved in a single operation to a cyclopentanol, or isomerized to cyclo-

(9) Trost, B. M.; Belletire, J. L.; Godleski, S.; McDougal, P.; Balkovec, J. M.; Baldwin, J. J.; Christy, M. E.; Ponticello, G. S.; Varga, S. L.; Springer, J. P. *J. Org. Chem.* **1986**, *51*, 2370.

(10) Also, see: Trost, B. M.; Miller, M. L. *J. Am. Chem. Soc.* **1988**, *110*, 3687.

(11) King, M. L.; Ching, C.; Ling, H.; Fujita, E.; Ochiai, M.; McPhail, A. T. *Chem. Commun.* **1982**, 1150. For a synthetic effort, see: Davey, A. E.; Taylor, R. J. K. *Chem. Commun.* **1987**, 25.

(12) Burgi, H. B.; Dunitz, J. D.; Shefter, E. *J. Am. Chem. Soc.* **1973**, *95*, 5065.

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pentenes. The ready availability of (+)- and (−)-ephedrine translates this strategy into a practical asymmetric synthesis of either enantiomeric cyclopentyl series.[14,15]

Acknowledgment. We thank the National Institutes of Health for their generous support of our programs. Mass spectra were gratefully provided by the Mass Spectrometry Facility, University of California-San Francisco, supported by the NIH Division of Research Resources.

(14) For use of chiral sulfoxides, see: Chaigne, F.; Gotteland, J. P.; Malacria, M. *Tetrahedron Lett.* **1989**, *30*, 1803.

(15) All new compounds reported herein have been fully characterized spectrally and elemental composition established by high resolution mass spectroscopy and/or combustion analysis.

Additions and Corrections

Current Contents on Diskette [*J. Am. Chem. Soc.* **1989**, *111*, 2747]. JAMES K. WHITESELL

The introductory paragraph now reads "List Price $600.00; ...;" it should read "J600 publication series for IBM and Macintosh $380.00; ...".

*Book Reviews**

Advances in Cycloaddition. Volume 1. Edited by Dennis P. Curran (University of Pittsburgh). JAI: Greenwich. 1988. xii + 189 pp. $34.25. ISBN 0-89232-861-4.

This volume contains five articles in which various aspects of 1,3-dipolar cycloadditions are reviewed. The first, "Steric Course and Mechanism of 1,3-Dipolar Cycloadditions" (31 pp) by R. Huisgen, takes the reader from the early to the latest stereochemical and kinetic probes and includes examples of stepwise cycloadditions. In the second, E. Vedejs reviews the preparation and cycloadditions of "Nonstabilized Azomethine Ylides" (19 pp). The third, by A. G. Schultz, is a review of "Molecular Rearrangements Occurring from Products of Intramolecular 1,3-Dipolar Cycloaddition:—", including azide, nitrone, and diazoalkane dipoles (33 pp). P. DeShong, S. W. Lander, Jr., J. M. Leginus, and C. M. Dicken coauthored the fourth review, "Dipolar Cycloadditions of Nitrones with Vinyl Ethers and Silane Derivatives" (42 pp). The last and longest review (61 pp), "The Cycloadditive Approach to β-Hydroxy Carbonyls:—", is by D. P. Curran and provides an overview of an alternative to the aldol condensation strategy.

This volume is highly recommended to all those who want to stay abreast of developments in the mechanisms and synthetic applications of 1,3-dipolar cycloaddition reactions. The writers have realized a good balance between the summary of achievements and the reporting of gaps in understanding or remaining synthetic challenges. The articles are well written, they are amply illustrated with equations or schemes, and they cover the literature into or through 1986.

J. Warkentin, *McMaster University*

Advances in Chemistry Series 218: Electronic and Photonic Applications of Polymers. Edited by M. J. Bowden (Bell Communications Research) and S. R. Turner (Eastman Kodak Company). American Chemical Society: Washington, D.C. 1988. XIV + 372 pp. $94.95. ISBN 0-8412-1400-X.

This highly recommended book was developed from a symposium similarly titled, sponsored by the Division of Polymeric Materials: Science and Engineering (PMSE), held at the 192nd Meeting of the American Chemical Society in Anaheim, California, September 7–12, 1986. As mentioned in the Preface, the plenary lectures from that Symposium provided the basis for this book. The contributed papers from the plenary sessions were published in a companion book as ACS Symposium Series No. 346, *Polymers for High Technology: Electronics and Photonics*.

Let me not delay in acclaiming this book as an intelligent, well organized, superbly written, and timely resource. The contents are divided into seven chapters, each one of which provides an in-depth yet highly readable account of a pertinent subject area authored by experts in that field. The entire book is profusely illustrated with creative plots, figures, photos, sketches, molecular structures, and tables which promote understanding. This volume also boasts 613 references to the literature, thus serving as an invaluable review and resource book for any current or prospective worker in this field. However, maybe the most appealing feature of this book is its pedagogical and unpresuming approach in introducing and developing each subject. While it is clearly targeted at an informed or expert audience, this book is easily digestible by the beginner, thanks to the paced introductions and illuminating illustrations that fill each chapter.

Chapter 1, Polymers for Electronics and Photonic Applications (M. J. Bowden), provides an informative overview of each subject covered in the remaining six chapters. The Chapter highlights the role of polymers in relevant high-technology areas, including microlithography, packaging, conducting polymers, molecular electronics, optical fiber coatings, integrated optics, nonlinear optics, and optical recording. The clear, concise writing style and captivating illustrations in Chapter 1 are highly compelling and encourage one to read further. This reviewer also appreciated the section Abbreviations and Symbols at the end of this (and several later) chapters.

Chapter 2, Organic Resist Materials (C. G. Willson and M. T. Bowden), reviews recent developments in applications of polymers as resists in microlithography designed to extend into the submicrometer regime and to maintain dominance in commercial manufacture of integrated circuits. Chapter 3, Materials and Processes for Deep-UV Lithography (T. Iwayanagi, T. Ueno, S. Nonogaki, H. Ito, and C. G. Willson), reviews in great detail resist materials and processes designed to support high-resolution deep-UV (DUV) lithography. Chapter 3 is easily the longest (116 pp) and most highly annotated (225 references) chapter in the book. Chapter 4, Molecular Electronics Using Langmuir-Blodgett Films (G. C. Roberts), provides a clear introduction to the preparation of LB films and describes their potential applications in the field of electronics, particularly those relying on the highly nonlinear properties of supermolecular assemblies. Chapter 5, Progress Toward Processable, Envi-

*Unsigned book reviews are by the Book Review Editor.