was selectively converted into the allylic alcohol **19** (88%) via the 2,3-sigmatropic shift of a selenoxide with bonding to the more accessible alkene β-face. Finally, MCPBA oxidation (77%) and thermal sulfoxide elimination (135 °C, xylene, $CaCO_3$ buffer) gave *d,l*-zygosporin E (52% isolated), identical with natural material according to spectroscopic and chromatographic data.[10,11] None of the isomeric (*Z*)-olefin was detected.[12] The same sequence of steps from **16** produced *d,l*-16-*epi*-zygosporin E, **20**, 70% yield for sulfoxide pyrolysis and 44% overall from **16**.[11]

The synthesis of zygosporin E illustrates the use of sulfide bridge stereochemistry as a relay for stereochemical information in medium-sized rings. High selectivity at eight of the nine asymmetric centers in **1** has been achieved. More important, the synthesis demonstrates that remote stereocontrol in a complex macrocycle is not restricted to the coupling of optically pure subunits.[5c,13]

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Registry No. **1**, 114651-74-0; 4, 90741-78-9; **5**, 114634-51-4; 6, 114634-52-5; **7**, 114634-53-6; **8**, 114634-54-7; **11**, 114634-55-8; **12**, 114634-56-9; **13**, 114634-57-0; **14**, 114634-58-1; **15**, 114651-83-1; **16**, 114651-84-2; **18**, 114634-61-6; **19**, 114634-62-7; **20**, 114634-63-8; $PhSeSe^+(CH_3)PhBFu^-$, 114634-60-5.

Supplementary Material Available: Analytical and spectral data for compounds **5–8**, **11–16**, **18–20**, and **1** (6 pages). Ordering information is given on any current masthead page.

(10) We are grateful to Dr. H. Minato for a comparison sample of natural zygosporin E.
(11) Characterization data for key intermediates, see: Supplementary Material.
(12) A byproduct tentatively identified as the enol acetate resulting from the other regiochemistry of sulfoxide elimination was also formed.
(13) Recent examples: Still, W. C.; Novack, V. J. *J. Am. Chem. Soc.* **1984**, *106*, 1148. Still, W. C.; Romero, A. G. *J. Am. Chem. Soc.* **1986**, *108*, 2105. Schreiber, S. L.; Sammakia, T.; Hulin, B.; Schulte, G. *J. Am. Chem. Soc.* **1986**, *108*, 2106. Vedejs, E.; Buchanan, R. A.; Conrad, P.; Meier, G. P.; Mullins, M. J.; Watanabe, Y. *J. Am. Chem. Soc.* **1987**, *109*, 5878.

Highly Efficient Synthesis of Carbacyclin Analogue. Stereospecific Synthesis of Aryl-Substituted Exocyclic Olefin[1]

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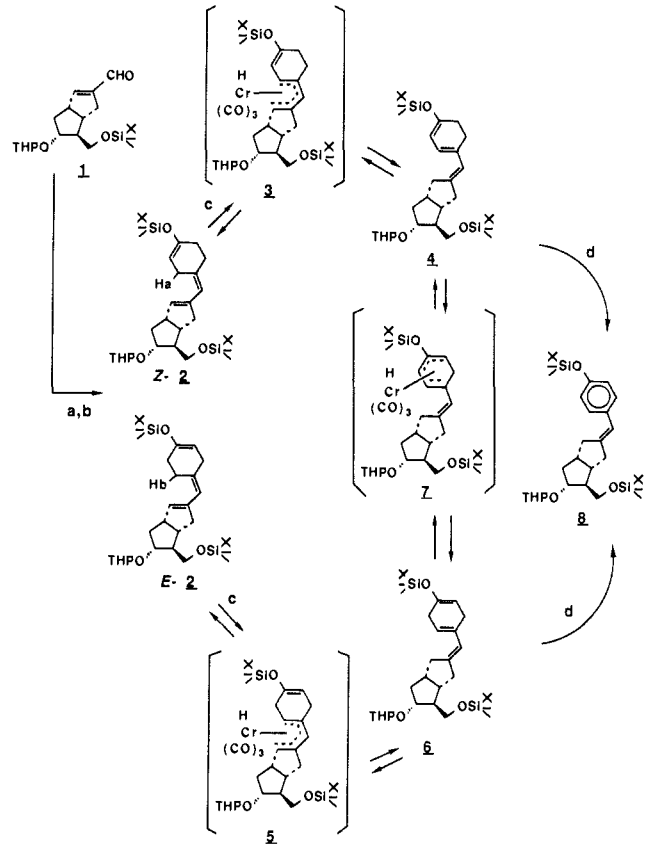
Although exocyclic olefins are now readily available in a stereocontrolled manner,[2] the stereospecific synthesis of aryl-substituted exocyclic olefins[3] still remains a challenging problem in organic synthesis.[4] A few years ago, on the basis of molecular design, we took an interest in the synthesis of the carbacyclin analogue with an aryl-substituted exocyclic olefin **13**. In this

Scheme I[a]



[a] (a) TBDMSO—⟨⟩—SO_2tol, *n*-BuLi, THF, −52 °C, then Ac_2O; (b) Na–Hg (5%), NaH_2PO_4, MeOH; (c) (naphthalene)$Cr(CO)_3$, acetone, 19 °C; (d) MnO_2, molecular sieves 4Å, benzene, reflux.

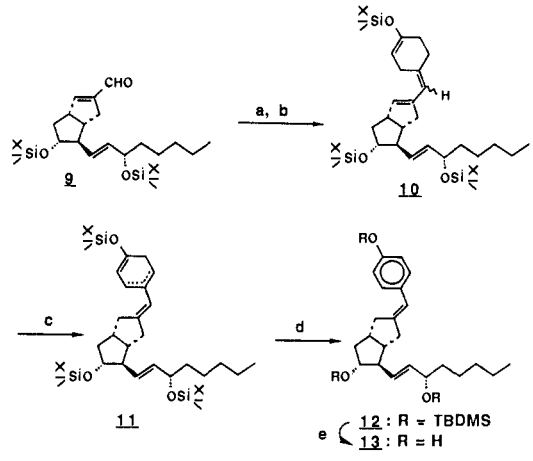
communications we wish to report a stereospecific synthesis of the various simple molecules **18**, **19**, **20**, **21**, **24**, and **25** as well as a highly stereoselective synthesis of **13**.

In the synthesis of carbacyclin by (methyl benzoate)$Cr(CO)_3$ catalyzed 1,4-hydrogenation reaction, we had already detected the stereo- and regiocontrolled 1,5-hydrogen shift of the conjugated diene, which proceeds at 130 °C via the U-shaped η^5-pentadienyl hydride intermediate with 18-electron configuration.[5,6] Furthermore, very recently, we found that this isomerization reaction proceeds smoothly even at 20 °C by the use of (naphthalene)-$Cr(CO)_3$ as a catalyst. On the basis of the argument described above, it was envisioned that both of (*Z*)-**2** and (*E*)-**2** would be converted to **8** stereospecifically by (naphthalene)$Cr(CO)_3$ catalyzed isomerization followed by aromatization. Thus a mixture of (*Z*)-**2** and (*E*)-**2** was first synthesized from the enal **1**, obtainable from the Corey lactone in a stereo- and regiocontrolled manner (ca. 70% overall yield),[7] via a three-step sequence of reactions (73%, (*Z*)-**2**:(*E*)-**2** = ca. 1:1). It was expected that (*Z*)-**2** would be isomerized to the most stable **4** in a stereo- and regiocontrolled manner through the U-shaped η^5-intermediate **3** generated by abstraction of the hydrogen Ha. Likewise, (*E*)-**2** was anticipated to be first isomerized to **6** through **5** formed by abstraction of the hydrogen Hb. We further expected that **6** would be isomerized to **4**, because it is known that cyclic 1,4-dienes are converted to 1,3-dienes by (arene)$Cr(CO)_3$ complexes.[8] Namely, regardless

(1) Dedicated to Professor E. J. Corey on the occasion of his 60th birthday.
(2) (a) Shibasaki, M.; Sodeoka, M.; Ogawa, Y. *J. Org. Chem.* **1984**, *49*, 4096. (b) Overman, L. E. In *Lect. Heterocycl. Chem.* **1985**, *8*, 59. (c) Corey, E. J.; Seibel, W. L. *Tetrahedron Lett.* **1986**, *27*, 905. (d) Hutchinson, D. K.; Fuchs, P. L. *J. Am. Chem. Soc.* **1987**, *109*, 4755. (e) Negishi, E. *Acc. Chem. Res.* **1987**, *20*, 65. (f) Liebeskind, L. S.; Mitchell, D.; Foster, B. S. *J. Am. Chem. Soc.* **1987**, *109*, 7908.
(3) For interesting compounds having an aryl-substituted exocyclic olefin, see: (a) Mason, C. P.; Edwards, K. R.; Carlson, R. E.; Pignatello, J.; Gleason, F. K.; Wood, J. M. *Science (Washington, D. C.)* **1982**, *215*, 400. (b) Flohé, L.; Böhlke, H.; Frankus, E.; Kim, S.-M. A.; Lintz, W.; Loschen, G.; Michel, G.; Müller, B.; Schneider, J.; Seipp, U.; Vellenberg, W.; Wilsmann, K. *Arzneim.-Forsh./Drug Res. 33* **1983**, (II) Nr. 9. (c) Noyori, R.; Ohta, M.; Hsiao, Yi; Kitamura, M.; Ohta, T.; Takaya, H. *J. Am. Chem. Soc.* **1986**, *108*, 7117.
(4) Pd-catalyzed vinyl/aryl coupling might be one of the most promising methods for the stereospecific synthesis of aryl-substituted exocyclic olefins. However, unfortunately, no method for the stereospecific synthesis of exocyclic vinyl halides is available now.
(5) (a) See: ref 2a. (b) Tucker, J. R.; Riley, D. P. *J. Organomet. Chem.* **1985**, *275*, 49.
(6) The 1,5-hydrogen shift of conjugated dienes catalyzed by (arene)$Cr(CO)_3$ complexes was already known. However, the stereochemistry of the reaction had been clarified by us,[2a] indicating that perfect formation of U-shaped η^5-pentadienyl hydride intermediates makes the complete stereochemical control of isomerized products possible.
(7) Sodeoka, M.; Shibasaki, M. *Chem. Lett.* **1984**, 579 (now commercially available from Nissan Chemical Industries, Ltd, Japan).

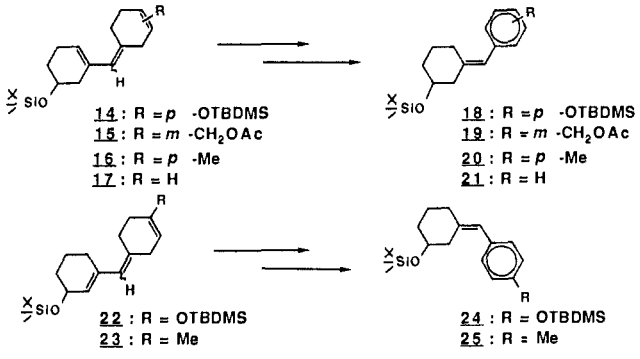
0002-7863/88/1510-4823$01.50/0

Scheme II[a]



[a] (a) TBDMSO—⟨⟩—SO_2tol, *n*-BuLi, THF, −50 °C, then Ac_2O; (b) Na-Hg (5%), NaH_2PO_4, MeOH; (c) (naphthalene)$Cr(CO)_3$, acetone, 19 °C; (d) MnO_2, molecular sieves 4Å, benzene reflux; (e) *n*-Bu_4NF, THF, room temperature.

Scheme III



of the stereochemistry of the starting triene **2**, only **4** was expected to be formed stereospecifically (Scheme I).

As expected, treatment of **2** (*E*:*Z* = ca. 1:1) with (naphthalene)$Cr(CO)_3$ (20 mol %) in acetone at 19 °C for 22 h (argon atmosphere) afforded a mixture of **4** and **6** in a ratio of 8:1 (100%), which was then converted to **8** (*E*) in 87% yield as a single product by reaction with activated MnO_2. The *Z*-isomer was also prepared from **8** by photochemical technique. In comparison of **8** with the Z-isomer, the stereospecificity of the present reaction was unequivocally confirmed. **8** should be the versatile key intermediate for **13** and the related compounds.[9,11]

The methodology described above was further applied to **10** having the ω-chain. The enal **9**[10] was transformed into **10** (79%, *E*:*Z* = ca. 1:1). Treatment of **10** with (naphthalene)$Cr(CO)_3$ (20 mol %) in acetone at 18–20 °C for 2 h gave a mixture of the isomerized products **11**, which underwent aromatization to give **12** stereospecifically (58% overall yield from **10**). The stereospecificity was confirmed by the same technique as described above. **12** was converted to **13**[11] (89%) by treatment with fluoride anion (Scheme II).

Finally it was found that the six-membered ring compounds with an aryl-substituted exocyclic olefin **18** (73%), **19** (76%), **20** (79%), **21** (73%), **24** (73%), and **25** (88%) could be also obtained stereospecifically from the corresponding partially conjugated trienes **14**, **15**, **16**, **17**, **22**, and **23** (in every case, *E*:*Z* = ca. 1:1), demonstrating the generality of the present methodology (Scheme III).

In conclusion, we have developed the conceptually new method for the stereospecific synthesis of aryl-substituted exocyclic olefins by utilizing the room temperature 1,5-hydrogen shift of conjugated dienes catalyzed by (naphthalene)$Cr(CO)_3$ complex. Further studies are in progress.

Supplementary Material Available: Experimental data for **1–8**, spectral data for **18** and **24**, and synthetic routes to **14**, **15**, **16**, **17**, **22**, and **23** (5 pages). Ordering information is given on any current masthead page.

Diastereoselective Photodeconjugation of α,β-Unsaturated Esters

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Ultraviolet light irradiation of aliphatic α,β-unsaturated esters having one hydrogen atom in the γ-position led to the corresponding deconjugated esters through a dienol intermediate.[2,3] This reaction was sufficiently general to be proposed as a synthetic procedure for the preparation of β,γ-unsaturated esters.[4] If the starting material bears one α-alkyl substituent, the dienol intermediate is prochiral, and we have shown precedently that enantioselective protonation of the α-carbon could be observed in an aprotic solvent containing small amounts of chiral aminoalcohols.[5] Thus, optically active β,γ-unsaturated esters were obtained through an asymmetric bimolecular reaction. A model involving a cyclic transition state was proposed to explain the chiral discrimination.[5b]

Photochemical studies of an intramolecular asymmetric induction in solution have been mainly restricted to photocycloadditions.[6,7] Thus, we chose to determine the importance of an

(1) As a former Corey's research group member, J.M. dedicates this paper in a tribute to E. J. Corey on the occasion of his 60th birthday.

(2) (a) Jorgenson, M. J. *Chem. Commun.* **1965**, 137. Jorgenson, M. J. *J. Am. Chem. Soc.* **1969**, *91*, 198. (b) Barltrop, J. A.; Wills, J. *Tetrahedron Lett.* **1968**, 4987. (c) Jorgenson, M. J.; Gundel, L. *Tetrahedron Lett.* **1968**, 4991. (d) Itoh, M.; Tokuda, M.; Kihara, K.; Suzuki, A. *Tetrahedron* **1968**, *24*, 6591. (e) Itoh, M.; Tokuda, M.; Seguchi, K.; Taniguchi, K.; Suzuki, A. *Kogyo Kagaku Zasshi* **1969**, *72*, 219.

(3) (a) Skinner, I. A.; Weedon, A. C. *Tetrahedron Lett.* **1983**, *24*, 4299. (b) Weedon, A. C. *Can. J. Chem.* **1984**, *62*, 1933. (c) Duhaime, R. M.; Lombardo, D. A.; Skinner, I. A.; Weedon, A. C. *J. Org. Chem.* **1985**, *50*, 873. (d) Marjerrison, M.; Weedon, A. C. *J. Photochem.* **1986**, *33*, 113.

(4) (a) Kropp, P. J.; Krauss, H. J. *J. Org. Chem.* **1967**, *32*, 3222. (b) Rando, R. R.; Doering, W. E. *J. Org. Chem.* **1968**, *33*, 1671. (c) Lombardo, D. A.; Weedon, A. C. *Tetrahedron Lett.* **1986**, *27*, 5555.

(5) (a) Mortezaei, R.; Henin, F.; Muzart, J.; Pete, J. P. *Tetrahedron Lett.* **1985**, *26*, 6079. (b) Mortezaei, R.; Piva, O.; Henin, F.; Muzart, J.; Pete, J. P. *Tetrahedron Lett.* **1986**, *27*, 2997. (c) Piva, O.; Henin, F.; Muzart, J.; Pete, J. P. *Tetrahedron Lett.* **1986**, *27*, 3001; **1987**, *28*, 4825.

(6) For reviews, see: (a) Kagan, H. B.; Fiaud, J. C. In *Topics in Stereochemistry*, Eliel, E. L., Allinger, N. C., Eds.; Wiley: 1977; Vol. 10, p 175. (b) Rau, H. *Chem. Rev.* **1983**, *83*, 535. (c) Griesbeck, A. G. *E.P.A. News* **1986**, *28*, 13.

(7) For asymmetric photocycloadditions, see: (a) Nehrings, A.; Sharf, H. D.; Runsink, J. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 877. (b) Koch, H.; Scharf, H. D.; Runsink, J.; Leismann, H. *Chem. Ber.* **1985**, *118*, 1485. (c) Herzog, H.; Koch, H.; Scharf, H. D.; Runsink, J. *Tetrahedron* **1986**, *42*, 3547. (d) Lange, G. L.; Decicco, C.; Tan, S. L.; Chamberlain, G. *Tetrahedron Lett.* **1985**, *26*, 4707. (e) Tolbert, L. M.; Ali, M. B. *J. Am. Chem. Soc.* **1985**, *107*, 4589. (f) Lange, G. L.; Lee, M. *Tetrahedron Lett.* **1985**, *26*, 6163. (g) Meyers, A. I.; Fleming, S. A. *J. Am. Chem. Soc.* **1986**, *108*, 306. (h) Demuth, M.; Palomer, A.; Sluma, H. D.; Dey, A. K.; Krüger, C.; Tsay, Y. H. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 1117. (i) Okado, K.; Samizo, F.; Oda, M. *Tetrahedron Lett.* **1987**, *28*, 3819. For other uses, see: (j) Schultz, A.; Kulkarni, Y. *J. Org. Chem.* **1984**, *49*, 5202. (k) Sudhakar, A.; Katz, T. J. *J. Am. Chem. Soc.* **1986**, *108*, 179. (l) Crich, D.; Davies, J. W. *Tetrahedron Lett.* **1987**, *28*, 4205. (m) Okada, K.; Sakai, H.; Oda, M.; Yoshimura, A.; Ohno, T. *J. Am. Chem. Soc.* **1987**, *109*, 5534.

(8) Frankel, E. N. *J. Catal.* **1972**, *24*, 358.

(9) For selective deprotection of alcoholic and phenolic silyl ethers, see: Collington, E. W.; Finch, H.; Smith, I. J. *Tetrahedron Lett.* **1985**, *26*, 681.

(10) Mase, T.; Sodeoka, M.; Shibasaki, M. *Tetrahedron Lett.* **1984**, *25*, 5087 (now commercially available from Nissan Chemical Industries, Ltd, Japan).

(11) Biological activities of **13** and the related compounds will be reported in due course.

0002-7863/88/1510-4824$01.50/0