ditions (0.02 M), keeping the **4**:**5** ratio nearly constant.[11] In the presence of n-Bu$_3$B (20 mol%) as a radical initiator[3e] (0.02 M, benzene, 25 °C, 24 h), the product distribution was not greatly affected, but the five- to six-membered ring ratio was somewhat improved: **4**:**5**:**6** = 76:5:19. The cyclization reactions were, therefore, carried out under the latter two dilution conditions.

The 1,2,3-all-cis stereochemistry in **4**, especially the high stereocontrol at the 3-position, is consistent with the approach of tin hydride from the less hindered convex side of the cis fused bicyclic system, as pointed out already by Stork.[2e,3b]

The mixture of products, containing the major five-membered ring product **4** (ca. 80%), was subjected without purification to further transformations of the cyclic vinylalkoxysilane moiety, some results being shown in Scheme II. Thus, the hydrogen peroxide oxidation[12] under the standard condition proceeded smoothly to form acetyl derivative **7** in 62% overall yield based on **3** in a stereochemically pure form. Basic cleavage[2f,13] and brominolysis[14] of the Si–alkenyl bond in **4** to the respective parent vinyl group (**8**) and 1-bromovinyl group (**9**) and cleavage of the Si–oxygen bond by methylation to the 1-trimethylsilylvinyl group (**10**) were also achieved. These results demonstrate that the present overall transformations are synthetically equivalent to the regio- and stereoselective hydroacylation and hydrovinylation of allylic alcohols, in which the acyl and vinyl groups are introduced onto the olefin carbon atom near the hydroxy group.

The hydroacylation has been applied to the bicyclic allyl alcohol derivative **11** to form the stereochemically pure **13** in high overall yield, as shown in Scheme III. The resulting ketone **13** should be an important intermediate for the total synthesis of vitamin D metabolites.[15]

A new stereochemical aspect characteristic of the 1-silylalkenyl radical cyclization has also been obtained. Thus, as shown in Scheme IV, the Z-rich (Si/R trans rich) mixture of the 1-bromo-1-octenylsilyl derivative **14**[16] gave, under similar conditions, the five-membered ring closure product **15** which had only the Z(Si/R cis) octenyl group. The result may be explained by rapid equilibration between the E- and Z-alkenyl radicals, the latter being sterically favored in the addition to olefin, as illustrated in Scheme V.[17] The product **15** could be converted into the E-octenyl derivative **17** by the basic desilylation procedure without loss of stereochemistry as well as into the 1-octanoyl derivative **16** by the hydrogen peroxide oxidation (Scheme IV).

Refinement and further applications are now under investigation.[18]

Acknowledgment. We thank Dr. M. R. Uskokovic for valuable discussions during his stay in Japan last November and H. Fujita for measurements of 400 MHz NMR.

Supplementary Material Available: Physical, spectroscopic, and selected analytical data for compounds **1**, **3**, **4**, **7**, **8**, **9**, **10**, **12**, **13**, **15**, **16**, and **17** (2 pages). Ordering information is given on any current masthead page.

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[11] The dependence of the product distribution on the reagent concentrations in the vinyl radical cyclization reactions has already been discussed in connection with the reversibility of the reaction.[3c,d]

[12] (a) Tamao, K.; Ishida, N.; Tanaka, T.; Kumada, M. *Organometallics* **1983**, *2*, 1694. (b) Tamao, K.; Ishida, N. *J. Organomet. Chem.* **1984**, *269*, C37. (c) Reference 1 and our previous works cited therein.

[13] (a) Price, C. C.; Sowa, J. R. *J. Org. Chem.* **1967**, *32*, 4126. (b) Hudrlik, P. F.; Hudrlik, A. M.; Kulkarni, A. K. *J. Am. Chem. Soc.* **1982**, *104*, 6809.

[14] Tamao, K.; Akita, M.; Maeda, K.; Kumada, M. *J. Org. Chem.* **1987**, *52*, 1100.

[15] The 4α epimer has been used for the total synthesis of calciferol derivatives: Baggiolini, E. G.; Iacobelli, J. A.; Hennessy, B. M.; Uskokovic, M. R. *J. Am. Chem. Soc.* **1982**, *104*, 2945.

[16] The corresponding chlorosilane as the silylating agent was prepared from (Z)-1-octenyldimethylethoxysilane by bromination and dehydrobromination, followed by treatment with acetyl chloride for ethoxysilane to chlorosilane conversion.

[17] Similar observations have been described for cyclization of 2-stannylalkenyl radicals.[3e,f]

[18] The silylvinyl radical cyclization has also been applied to acyclic allyl alcohols; the regio- and stereochemical studies are currently underway.

Determination of the Absolute Steric Course of a Solid-State Photorearrangement by Anomalous Dispersion X-ray Crystallography

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An interesting situation arises when compounds that rearrange through multiply degenerate reaction pathways in solution are studied in the solid state. In general, the degeneracy will be lifted in the crystal owing to its anisotropic environment, and the problem then becomes one of determining the extent to which each of the degenerate (solution) mechanisms contributes to the overall solid-state process. By solving such problems we learn much about the forces that control reactivity in molecular crystals. In this communication we report the case of a rearrangement that is 4-fold degenerate in solution but which follows a single mechanism in the crystal.

The reaction studied was the di-π-methane photorearrangement of dibenzobarrelene-11,12-diester **1** to the dibenzosemibullvalene derivative **4**.[1] This reaction occurs both in solution and the solid state, and its commonly accepted mechanism (path I) is shown in Scheme I.[2a] It is readily apparent that there are three additional and equivalent pathways (II–IV) for a total mechanistic degeneracy of four.

The approach to be taken in determining the relative importance of these four pathways to the solid-state rearrangement came from the realization that paths I and II lead to one enantiomer of **4**, whereas pathways III and IV give the other. Fortuitously, diester **1** crystallizes in a homochiral conformation in the chiral space group $P2_12_12_1$ and, as reported by us earlier,[1] undergoes stereospecific photorearrangement in the solid state to afford **4** in quantitative enantiomeric excess. This result establishes complete (I + II) vs (III + IV) discrimination in the crystal but does not differentiate between the two possibilities; neither does it indicate the relative importance of path I vs path II (or path III vs path IV).

In principle, it is possible to differentiate between pathways (I + II) and (III + IV) by determining the absolute configuration of the molecules in a reactant crystal and correlating this with the absolute configuration of the photoproduct generated by irradiation of that same crystal. To this end, a fragment of a large (55 mg) crystal of **1** was subjected to X-ray crystal structure analysis, taking account of anomalous dispersion, as described originally by Bijvoet.[3] At the same time, the remaining fragment was photolyzed and shown to give levorotatory **4** ($[\alpha]_D = -25.4°$, CHCl$_3$). Recrystallization of this material from ethanol gave prisms (mp 124–125 °C, space group $P4_12_12$ or $P4_32_12$) suitable for Bijvoet analysis. In both cases the anomalous dispersion is small ($\Delta f'' = 0.009$ for carbon, 0.032 for oxygen), but Hamilton's R factor ratio test[4a] favored one chirality for **1** and space group

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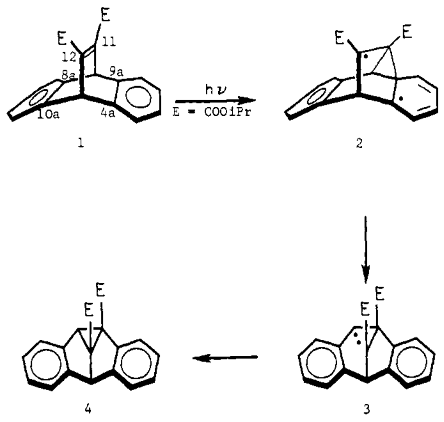
[1] Evans, S. V.; Garcia-Garibay, M.; Omkaram, N.; Scheffer, J. R.; Trotter, J.; Wireko, F. *J. Am. Chem. Soc.* **1986**, *108*, 5648. The first example of this type of photorearrangement in solution (that of barrelene to semibullvalene) was reported by Zimmerman et al. (Zimmerman, H. E.; Grunewald, G. L. *J. Am. Chem. Soc.* **1966**, *88*, 183). The first example of a solution phase dibenzobarrelene to dibenzosemibullvalene rearrangement was reported for the dimethyl diester of **1** by Ciganek (Ciganek, E. *J. Am. Chem. Soc.* **1966**, *88*, 2882).

[2] (a) Zimmerman, H. E. In *Rearrangements in Ground and Excited States*; de Mayo, P., Ed.; Academic: New York, 1980; Vol. 3, Chapter 16. The debate over whether 1,4-biradicals such as **2** represent true minima on the di-π-methane hypersurface [see (b) Paquette, L. A.; Bay, E. *J. Org. Chem.* **1982**, *47*, 4597. (c) Adam, W.; Dorr, M.; Kron, J.; Rosenthal, R. J. *J. Am. Chem. Soc.* **1987**, *109*, 7074. (d) Zimmerman, H. E.; Kamath, A. P. *J. Am. Chem. Soc.* **1988**, *110*, 900] does not affect the arguments presented in this paper.

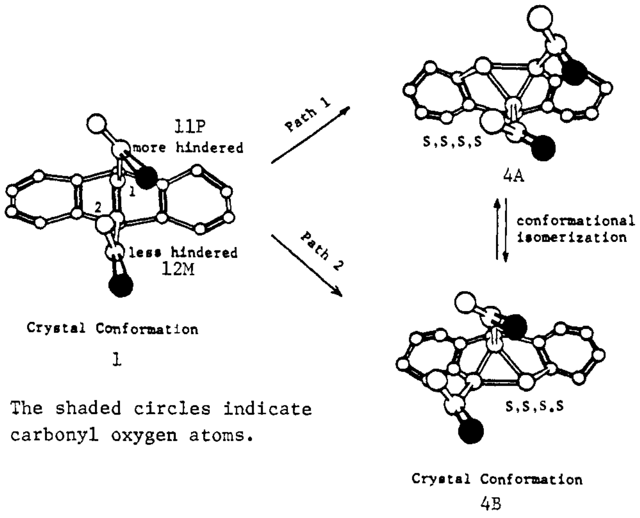
[3] Bijvoet, J. M.; Peerdeman, A. F.; Van Bommel, J. A. *Nature* **1951**, *168*, 271.

Scheme I



Path I: initial 9a-11 bonding
Path II: initial 10a-12 bonding
Path III: initial 4a-12 bonding
Path IV: initial 8a-11 bonding

Scheme II



The shaded circles indicate carbonyl oxygen atoms.

$P4_32_12$ for **4** at confidence levels of about 95%. Since this test may not be completely reliable in this situation,[4b] further comparisons were made by using the Bijvoet difference method.[3,4c,d] Among Friedel pairs with the largest expected intensity differences, 20 (out of 30) for **1** and 14 (out of 20) for **4** indicated the same absolute configurations as Hamilton's test. Hence, we are reasonably confident that the correct absolute configurations have been assigned. The crystal of **1** studied contained molecules with the 11P, 12M absolute configuration,[5] and its photoproduct had the *S,S,S,S*-(−) configuration. Ball and stick drawings of these absolute configurations are shown in Scheme II.

The first conclusion to be drawn from the results is that pathways I and/or II are followed; pathways III and/or IV would have given the *R,R,R,R*-(+) photoproduct. In terms of structure, the 11P, 12M conformation of **1** predicts that paths III and/or IV would involve severe clashing of the ester groups as they are forced toward each other during the initial stages of reaction. In contrast, paths I and/or II involve movement of the ester groups *away* from one another, thus providing a plausible rationale for the observed results. Two questions arise at this point: (a) with the data in hand, can we determine the relative importance of paths I and II and (b) can we identify the crystal forces that control the preferred pathway(s)? The answer to both questions is a qualified yes. Two pieces of evidence indicate that path II is favored over path I. First, the packing diagram shows that *the ester group 12M, which is attached to the vinyl carbon atom involved in path II, is in a much freer lattice environment than its path I counterpart*. Because the ester group attached to the reactive site is required to move most during the initial stages of the rearrangement, there is a clear prediction of a preference for path II. This qualitative conclusion is borne out quantitatively by packing potential energy calculations of the type previously reported,[6] which simulate the steric interactions developed between the host lattice and guest reactant during the early stages of rearrangement. Secondly, assuming a least motion (topochemical) process,[7] pathway II produces the photoproduct **4** *directly in its final crystal conformation 4B*; in contrast, topochemical reaction via path I would lead to the unobserved conformer 4A.[8]

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Supplementary Material Available: Stereodiagram of diester **1** showing the difference in local packing density around each of the ester groups and a table of Bijvoet measurements from which absolute configurations were determined (2 pages). Ordering information is given on any current masthead page.

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(4) (a) Hamilton, W. C. *Acta Crystallogr.* **1965**, *18*, 502. (b) Rogers, D. *Acta Crystallogr.* **1981**, A*37*, 734. (c) Hope, H.; de la Camp, U. *Acta Crystallogr.* **1972**, A*28*, 201. (d) Pennington, W. T.; Chakrabory, S.; Paul, I. C.; Curtin, D. Y. *J. Am. Chem. Soc.* **1988**, *110*, 6498.

(5) The designation 11P, 12M uses the conformational chirality formalism for describing absolute configuration. See: Cahn, R. S.; Ingold, C.; Prelog, V. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 385.

(6) Similar calculations account for the striking *regioselectivity* observed in the solid-state di-π-methane rearrangement of a series of unsymmetrically substituted dibenzobarrelene-11,12-diesters. See: Garcia-Garibay, M.; Scheffer, J. R.; Trotter, J.; Wireko, F. *Tetrahedron Lett.* **1988**, *29*, 2041. Scheffer, J. R.; Trotter, J.; Garcia-Garibay, M.; Wireko, F. *Mol. Cryst. Liq. Cryst. Inc. Nonlin. Opt.* **1988**, *156*, 63. We note that path I is slightly favored over path II by radical stability considerations (radical placement next to the more conjugated ester). However, the work referred to above has shown that radical stability arguments are *not* generally predictive for these systems.

(7) (a) Cohen, M. D.; Schmidt, G. M. J. *J. Chem. Soc.* **1964**, 1996. (b) Cohen, M. D. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 386.

(8) We cannot completely rule out the possibility that reaction occurs via path I followed by isomerization of the higher energy (MM2) conformer 4A to the lower energy conformer 4B during workup and recrystallization. This does not, however, affect the basic conclusion regarding the preference for pathways I and/or II over III and/or IV in the solid state.

Potential Precursors to Electronic Materials: Three-Coordinate Cd in $[\mathrm{MeCd}(\mu\text{-}t\text{-}\mathrm{Bu_2P})]_3$, the First Cadmium Diorganophosphide

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As part of a program focused on the design and synthesis of precursors for electronic materials we[2] and others[3] recently demonstrated the use of single source molecules for the growth of III/V

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(2) Cowley, A. H.; Benac, B. L.; Ekerdt, J. G.; Jones, R. A.; Kidd, K. B.; Lee, J. Y.; Miller, J. E. *J. Am. Chem. Soc.* **1988**, *110*, 6248.

(3) Bradley, D. C.; Faktor, M. M.; White, E. A. D.; Frigo, D. M. U.K. Patent No. 8703227. Andrews, D. A.; Davies, G. J.; Bradley, D. C.; Faktor, M. M.; Frigo, D. M.; White, E. A. D. *Semicond. Sci. Technol.* **1988**, *3*, 1053. See, also: Bradley, D. C.; Faktor, M. M.; Frigo, D. M.; Young, K. V. *Chemtronics* **1988**, *3*, 50. Andrews, D. A.; Davies, G. J.; Bradley, D. C.; Faktor, M. M.; Frigo, D. M.; White E. A. D. *Semicond. Sci. Technol.* **1988**, *3*, 1053.

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