In suitably functionalized 1,5-dienes, cyclooligomerization occurs to some extent (substrate **10**). In previous studies we have established that this process dominates when terminal 1,5- and 1,6-dienes are employed.[17] Finally, selected functional groups (substrates **5d**, **5e**) totally inhibit the reaction. Irreversible reaction of the catalyst with these functional groups is probably responsible for these results, although studies are still underway to determine precisely the reason for failure in these cases.

In summary, excellent results have been obtained for the organoyttrium-catalyzed reductive hydrogenation of substituted dienes. The facile process that has been developed provides excellent selectivities and yields. Although nominal total reduction and competing cyclization occurs in selected diene substrates using the current protocol, further studies designed to optimize the organometallic catalyst by both "ligand tuning" and "metal tuning" are expected to resolve these problems.

Acknowledgment. We thank the National Institutes of Health for their generous support of this research.

Supplementary Material Available: Complete experimental details and spectral data for all the hydrogenation reactions described herein (33 pages). Ordering information is given on any current masthead page.

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Photosensitized Pyrimidine Dimer Splitting by a Methoxyindole Bound to a Dimer-Recognizing Macrocycle

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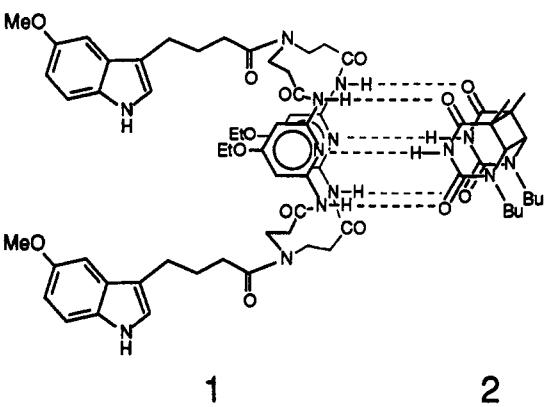
Summary: A macrocycle has been prepared that binds to a pyrimidine dimer by hydrogen bonding and photosplits the bound dimer with quantum efficiency greater than 0.1 in both protic and aprotic solvents.

Mimicry of enzyme-mediated photorepair of pyrimidine dimers in DNA by simple organic systems offers to both demystify and enhance the appreciation for the natural repair enzymes, the photolyases.[1] These enzymes photosplit dimers that arise in DNA from exposure to ultraviolet light. We recently devised and synthesized a macrocycle[2] that binds to pyrimidine dimers by use of the characteristic hydrogen-bonding pattern of the dimer as a recognition[3a,b] motif. The macrocycle employed two diaminopyridines[3c] for complexation to the dimer and an indole as photosensitizer. Although the macrocycle sensitized dimer splitting, the quantum yield was low ($\Phi \simeq 0.01$ in CH_3CN), and the mode of sensitization could not be identified due to overlap of diaminopyridine and indole absorption bands. We now report that a new macrocycle **1**, with well-separated absorption bands of sensitizer and recognition components, induces cycloreversion of the complexed dimer **2** (Chart I) upon excitation of the sensitizer.[4] Quantum efficiency was significantly higher ($\Phi = 0.11$ in acetonitrile) than the previous macrocycle. Also, complexation and splitting were found to occur in a protic solvent, in spite of the tendency of such solvents to disrupt hydrogen-bonded complexes.

Chart I



1 **2**

The absorption band of the diaminopyridine, which is required for recognition, was separated from the sensitizer's band by use of substituents. The γ-ethoxy group on the diaminopyridine resulted in a blue shift in the absorption band (red edge < 300 nm), as well as tighter binding;[2,5] a 5-methoxy group on the indole resulted in a red shift in the sensitizer's absorption band (red edge > 320 nm). Irradiation[6] at 313 nm resulted in virtually sole excitation of the methoxyindole, with little or no direct excitation of

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(4) The synthesis of **1** will be presented elsewhere (see supplementary material). High-resolution FAB MS and ^{1}H-NMR spectra were consistent with the assigned structure (e.g., high-resolution FAB MS of **1**: theoretical exact mass for $C_{52}H_{62}N_{10}O_{10} + H^+$ 987.4729, found 987.4742).

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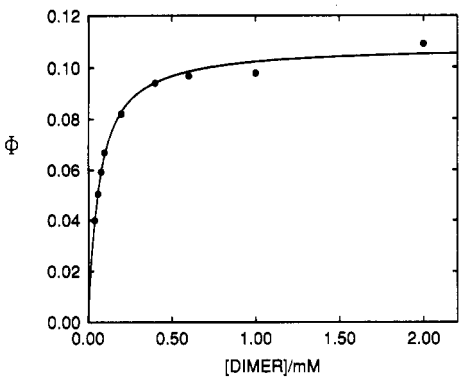

Figure 1. Dependence of quantum efficiency of splitting on concentration of **2** in acetonitrile (21 μM **1**; λ_{irr} = 313 nm). Data points are the average of two determinations, which agreed within 5%.

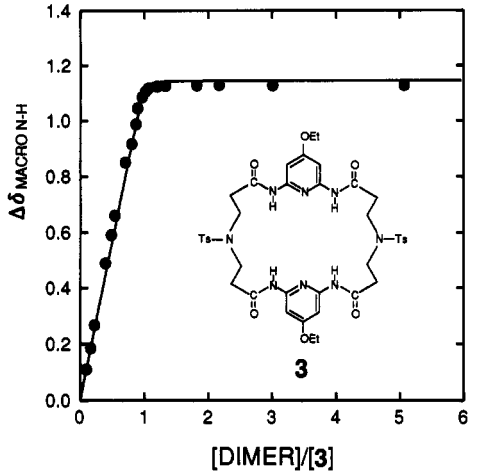

Figure 2. NMR titration of 7.1 mM **3** (structure shown) with **2** in $CDCl_3$ demonstrated formation of a complex with clear 1:1 stoichiometry, and $K_{assoc} \sim 10^5$ M^{-1} was estimated by curve fitting to the data shown. This analogue of **1** had a simpler NMR spectrum, which allowed changes in the chemical shifts of the N–H signals of the macrocycle to be unambiguously followed.

the diamino-γ-ethoxypyridine or the dimer.

Splitting efficiency of 1,1'-di(*n*-butyl)thymine cis-syn photodimer **2** by **1** was quantitated by UV absorption spectroscopy.[7] A value of Φ = 0.11 was determined at 2 mM **2** in acetonitrile (21 μM **1**). Only the product of splitting (1-butylthymine) was detected by HPLC. The quantum efficiency of splitting showed saturation in a titration experiment (Figure 1). The association constant of **1** and **2** was estimated at $1.8 \pm 0.1 \times 10^4$ M^{-1} by curve fitting to the data shown in Figure 1. This paralleled the NMR titration of **3**, an analogue of **1** that clearly formed a complex of 1:1 stoichiometry with **2** in $CDCl_3$ (Figure 2). Methyl substitution at the N(3) and N(3') positions of **2** (i.e., Me_2-**2**) prevented splitting by **1**, indicative of the role of hydrogen bonding in preassociation of dimer and macrocycle. At these low concentrations, failure of **1** and Me_2-**2** to preassociate precludes splitting.

Photosensitization of dimer splitting by **1** was even found to occur in methanol (containing 7% acetonitrile for macrocycle solubility; Figure 3). Binding was weaker than in the case of acetonitrile ($K_{assoc} \sim 2 \times 10^2$ M^{-1} by curve fitting to the data shown), presumably due to competition by solvent for hydrogen bonding to **1** and **2**. The failure of Me_2-**2** to undergo splitting in the same solvent was

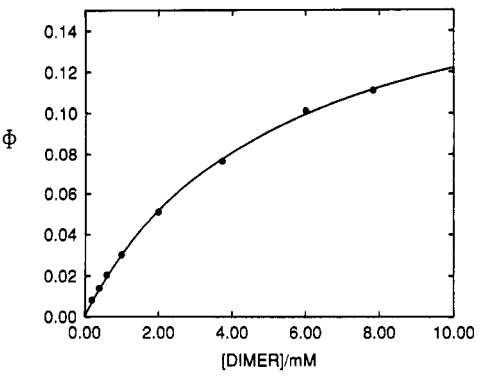

Figure 3. Dependence of quantum efficiency of splitting on concentration of **2** in methanol containing 7% acetonitrile (26 μM **1**; λ_{irr} = 313 nm). Data points are the average of at least two determinations, which agreed within 5%.

evidence that specific hydrogen bonding was required for splitting of **2** even in this protic solvent.[8] As a further test of the need for preassociation, two methoxyindoles not linked to a dimer-recognizing macrocycle were photolyzed in the presence of **2**. One, 4-(5-methoxyindol-3-yl)butanoic acid, was selected for its similarity to the macrocycle-bound indole of **1**, and it failed to sensitize splitting of **2** (at concentrations comparable to **1**) in acetonitrile or methanol–acetonitrile (93:7), confirming that preassociation of **1** and **2** is required for splitting. Additionally, 5-methoxytryptophol in methanol–acetonitrile (93:7) was also ineffective. The results were unchanged by Ar-purging of the solutions.

Splitting probably occurs as a result of photoinduced electron transfer from a 5-methoxyindolyl group of the macrocycle to the complexed dimer.[7,9,10] The resulting dimer radical anion then splits,[10,11] and charge recombination restores neutrality. It was found that **1** functioned photocatalytically, splitting approximately nine dimers during an extended irradiation in acetonitrile.[12]

The limiting values of Φ at saturating dimer concentration were approximately 0.11 for acetonitrile (ϵ = 37.5) and 0.18 for methanol (ϵ = 32.7) containing 7% acetonitrile (determined from curve fitting). A covalently linked dimer–methoxyindole system had previously been found to undergo intramolecularly photosensitized dimer splitting with comparable efficiencies (Φ = 0.14 in CH_3CN and 0.17 in CH_3OH).[9] The factor limiting splitting efficiency in the covalent system was thought to be back-electron transfer within the charge-separated species formed upon electron transfer from excited indole to dimer (i.e., $D^{\bullet-}$–$Ind^{\bullet+}$). Further studies of forward- and back-electron transfer rates in the complex of **1** and **2** are required to identify the factors that limit splitting efficiency in that system.

Dimer photosplitting by **1** in both protic and aprotic environments demonstrates that dimer recognition by hydrogen bonding allows noncovalently linked sensitizers

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(12) Approximately 60% of the activity remained after this irradiation.

to split dimers with efficiencies comparable to those found in systems with short, covalent linkers. If the behavior of methoxyindole is typical of electron-donating sensitizers (e.g., the reduced flavin[13] cofactor employed by photolyases), hydrogen bonding may be a viable dimer recognition motif available to photolyases.

Acknowledgment. We thank the National Institutes of Health (CA49729) and the Del E. Webb Foundation for financial support.

Supplementary Material Available: Experimental procedures, characterization data, and UV absorption spectra (7 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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1,4-Silyl Migration Reactions. Applicability to Alkyl-, Vinyl-, and Cyclopropylsilanes†

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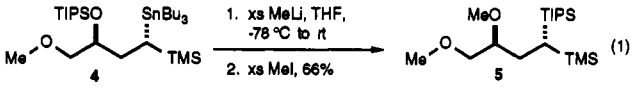
Summary: A series of silyl protected alcohols containing a tin substituent were found to undergo transmetalation followed by silyl migration from oxygen to carbon in the presence of methyllithium.

The utility of 1,1-dimetallo compounds as building blocks in organic synthesis has become increasingly apparent in the past few years.[2] Several papers have appeared describing the synthesis and reactivity of these compounds. Our interest in this area has focused on the preparation of dimetallo compounds of silicon and tin via hydrometalation reactions.[3]

We recently described a hydrometalation–stannylation sequence catalyzed by titanium for the stereoselective synthesis of γ-hydroxyvinylstannanes **A–C**, R, R′ = alkyl (Figure 1). These substrates were shown to undergo highly diasteroselective hydroxyl-directed hydrogenation and cyclopropanation reactions leading to novel heterobimetallic derivatives **2** and **3** (Figure 2).[4,5] Claisen rearrangement of a derivative of **1** was also explored leading to allylic dimetallo compounds.[6]

In order to evaluate the reactivity of the stereoisomeric silyl and stannyl compounds (i.e., M′ = Si, M = Sn) toward the abovementioned reactions, synthetic routes to these compounds were required. We report a particularly facile entry into silicon-containing compounds by taking advantage of a stereoselective 1,4-oxygen to carbon migration of a silyl group. Several different silyl groups were shown to migrate in high yield. We also report the first example of migration of a silicon to a cyclopropyl anion.

We first encountered a silyl migration during a study of the transmetalation of **4**. Our objective was to transmetalate the C–Sn bond then alkylate the resulting carbanion and determine if the remote methoxy group controlled the stereochemistry at the carbanionic center. A TBDMS group was chosen to minimize complexation to the oxygen at C-2. Instead, upon treatment of **4** with MeLi in THF followed by addition of methyl iodide, we isolated **5** in 66% yield as a 3:1 mixture of isomers. The major product arose from a 1,4-migration of the TIPS with retention of stereochemistry as determined by comparison of a related compound of known configuration.



(1)

Migration of silicon is a ubiquitous process.[7] The best studied of these reactions are the Brook- and retro-Brook-type 1,2-rearrangements.[8a,b] Higher order reactions are also known, although they are generally considered to be less facile. One study reports the relative ease of migration to be 1,2 > 1,3 ≫ 1,4 or 1,5.[8c,d] We considered that 1,4-rearrangement of silicon could represent a useful route for preparation of stereoisomeric silanes (Figure 3).[9]

The first example of a 1,4-rearrangement appears to be that reported by Speier.[10] Later, during a study of homoenolate equivalents, Evans established that the steric

† Dedicated to our colleague, and a seminal contributor to silicon migration chemistry, Professor Adrian Brook.

(1) (a) Fellow of the Alfred P. Sloan Foundation, 1991-1993, NSERC (Canada) University Research Fellow, 1987-1992. BioMega Young Investigator Awardee, 1990-1992. (b) Simcoe Scholar 1991-1993.

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