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Article

An Experimental Stereoselective Photochemical [1s,3s]-Sigmatropic Silyl Shift and the Existence of Silyl/Allyl Conical Intersections

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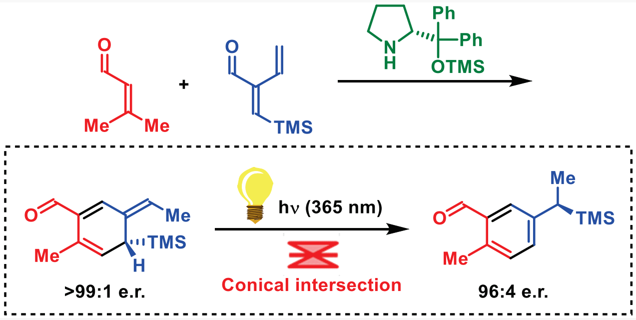
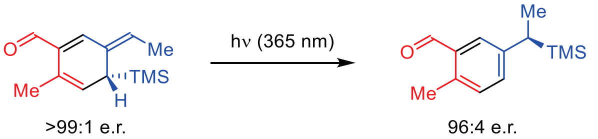
ABSTRACT: We report an experimental discovery and computational investigation of the first photochemical stereoselective [1,3]-sigmatropic silyl shift of an allylsilane. An organocatalytic enantioselective cascade annulation generates a trimethylsilyl-*o*-isotoluene reactant in >99:1 e.r., and this trimethylsilyl-*o*-isotoluene contains an allylic silane moiety that undergoes a stereoselective photochemical [1,3]-silyl shift to form a benzylsilane with 96:4 e.r. The mechanism of this unprecedented [1,3]-silyl shift has been elucidated by a series of experimental studies and CASSCF, DFT, and TD-DFT calculations on model systems and the experimental system. The highly stereoselective photoreaction is proposed to occur via a singlet silyl/allyl conical intersection. This is a new demonstration of the role of conical intersections in selective photochemistry.



INTRODUCTION

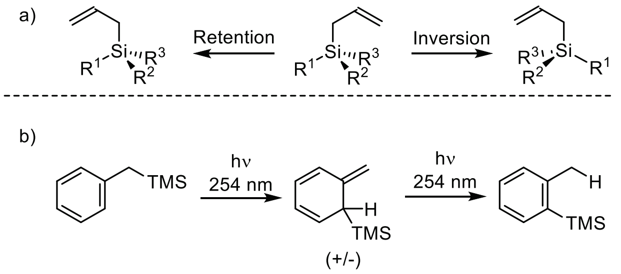
Metal-free enantioselective incorporation of silicon into organic molecules has traditionally only been achieved via NHC catalysis[1] and Arnold's recent directed evolution of enzymes to produce enantioenriched carbon−silicon compounds.[2] We have now discovered an organocatalytic reaction sequence leading to a stereoselective allylic silane formation, followed by a highly stereoselective photochemical [1,3]-silyl shift, constituting a novel approach to the formation of highly enantioenriched chiral benzylic silanes (Scheme 1).

Scheme 1. Unprecedented Stereoselective Photochemical [1,3]-Silyl Shift



Several [1,3]-sigmatropic shifts of allylic silyl groups have been studied previously, but often without stereochemical control. In 1972, Kwart and Slutsky observed a thermal [1,3]-silyl shift.[3] Subsequently, they recognized a [1i,3s] stereochemistry with inversion at silicon with aryl-substituted silicon.[3b,4] In 1997, theoretical studies performed by Takahashi and Kira, and by Yamaha et al., showed that the thermal [1,3]-sigmatropic shift could happen via two different transition states: one involves inversion of the stereocenter on silicon, while the other results in stereochemical retention (Scheme 2a).[5] Subsequently, the retention route [1r,3s] was found experimentally by Kira et al., who showed how the retention or inversion could be altered by substituents.[6] It is generally known that [1i,3s]-sigmatropic shifts are thermally allowed but geometrically difficult in hydrocarbons.[7] Photochemical [1,3]-sigmatropic shifts, mainly of H, but also of C, have been studied extensively with computational methods.[8b,9] The

Scheme 2. (a) Retention and Inversion of the Silicon Stereocenter in a [1,3]-Sigmatropic Shift of an Allylic Silyl Group, and (b) Photochemical [1,3]-Hydrogen Shift of a Silyl-*o*-isotoluene



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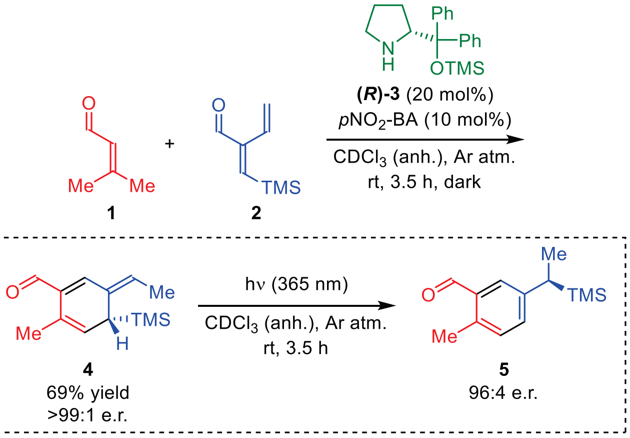
[1r,3s]-sigmatropic shift is allowed photochemically and is geometrically readily achieved.

There has been one example of a photochemical [1,3]-hydrogen shift in silyl-*o*-isotoluene, reported in 1985, and shown in Scheme 2b.[10a] TMS-*o*-isotoluene can be formed from irradiation of α-trimethylsilyltoluene. This isotoluene is a relatively stable molecule in the ground state, as a thermal [1,3]-hydrogen shift is symmetry forbidden unless happening in the geometrically impossible antarafacial manner. A [1,3]-hydrogen shift occurs upon irradiation of the TMS-*o*-isotoluene at 254 nm UV light, but no mention of migration of the TMS group is made (Scheme 2b). However, since the silyl-*o*-isotoluene is generated photochemically from benzyltrimethylsilane, the [1,3]-silyl shift may not have been recognized.

We report a novel organocatalytic enantioselective annulation, coupled with the first photochemical stereoselective [1,3]-sigmatropic silyl shift of an allylsilane, by which the TMS group in the optically active silyl-*o*-isotoluene **4** (>99:1 e.r.) undergoes a stereoselective photochemical [1,3]-silyl shift, forming a benzylsilane **5** in 96:4 e.r. (Scheme 3). A series of experimental and computational investigations have been performed in order to elucidate the mechanism of this novel photochemical [1,3]-silyl shift.

Scheme 3. Organocatalytic Enantioselective Cascade Reaction for the Formation of Silyl-*o*-isotoluene 4 and the Stereoselective Photochemical [1,3]-Silyl Shift[a]



[a]The enantiomeric ratio is measured for the thiosemicarbazone-derivatized product using (*R*)-**3** as the catalyst (see Supporting Information).

RESULTS AND DISCUSSION

Experimental Studies. The reaction between 3-methylcrotonaldehyde **1** and oxadendralene **2** in the presence of 20 mol % diphenylprolinol silyl ether catalyst (*R*)-**3**[11] and 10 mol % *p*-nitrobenzoic acid affords silyl-*o*-isotoluene **4** with a >99:1 e.r. (Scheme 3). Subsequently, irradiation of the *crude* mixture containing **4** (3 × 3 W, 365 ± 5 nm) leads to the photochemical [1,3]-silyl shift, yielding the desired benzylsilane **5** in 61% yield and 91:9 e.r. (*vide infra* and see Supporting Information for reaction optimization).

The reaction can be performed instead as a two-step procedure: First, silyl-*o*-isotoluene **4** can be isolated in 69% yield and >99:1 e.r. Subsequent irradiation of **4** gives benzylsilane **5** in a 96:4 e.r. (Scheme 3, bottom). Tables S1 and S2 in the Supporting Information provide an extensive screening of acid additives and solvents.

Based on a combination of reports on conjugate additions to oxadendralenes,[12] we propose the reaction mechanism in Scheme 4 for the enantioselective cascade involving an aminocatalytic dienamine-mediated cyclization and a subsequent photochemical [1,3]-silyl shift.

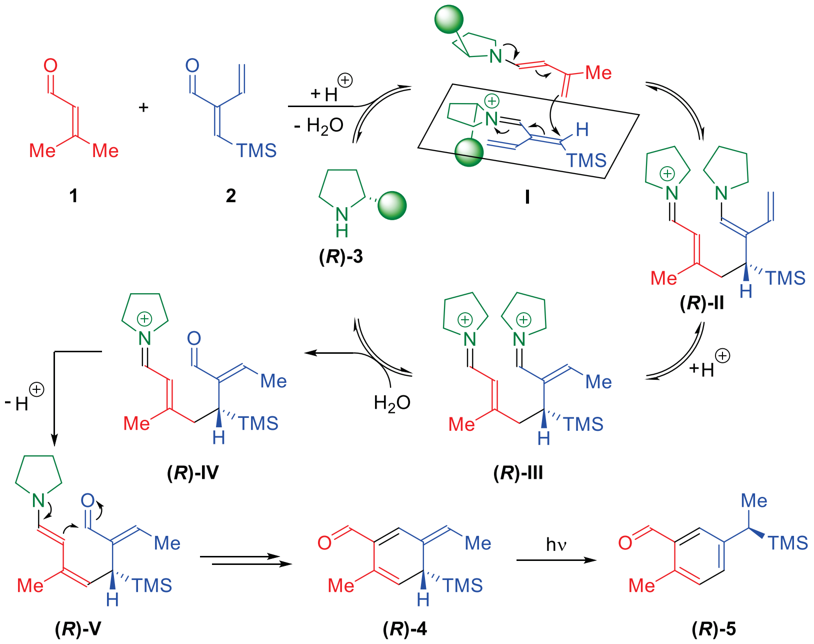
In the first step, the diarylprolinol silyl ether catalyst (shown as the (*R*)-**3** catalyst) facilitates the formation of a reactive dienamine by condensation and isomerization with 3-methylcrotonaldehyde **1**. A concurrent pathway forms the iminium ion of **2**, thereby enabling an enantioselective 1,4-conjugate addition. In the case of organocatalytic dual activation, we propose that the Michael addition proceeds as depicted in **I**. As shown, the *s-cis*-dienamine is expected to approach from the top face in order to account for steric repulsion between the two catalysts and the TMS group situated in the β-position of the iminium ion derived from oxadendralene **2**. The resulting product (*R*)-**II** equilibrates into the iminium ion (*R*)-**III**, which upon hydrolysis forms (*R*)-**IV**. Finally, an enamine-mediated intramolecular aldol condensation and elimination affords the silyl-*o*-isotoluene intermediate (*R*)-**4**, which is set up for a photochemical [1,3]-silyl shift which forms the optically active benzylsilane (*R*)-**5**. The absolute configuration of **5** was assigned with CD (both experimentally and computationally, see Supporting Information) and is in agreement with the proposed mechanism in Scheme 4.

Notably, the geometry of the ground state silyl-*o*-isotoluene **4** was found to be *Z* and *s-cis* with respect to the exocyclic C=C double bond and the aldehyde functionality, respectively (see Supporting Information). This was found experimentally by a NOESY spectrum and supported by computational studies (*vide infra*). We presume that the *Z*-configuration is set going from **II** to **III**, following a rotation around the exocyclic α- and β-carbon bonds. The conjugation of the unsaturated aldehyde π-system is optimal in this linear form and must compensate for the increased steric clash between the aldehyde and the *o*-methyl group and between the allyl and TMS groups.

In order to test for the existence of free radicals in the photochemical reaction, radical traps (TEMPO, BHT) in excess were added to the reaction mixture (see Supporting Information). Radical traps would be expected to react with any transient radical formed in the reaction mixture, but no adducts of radical traps and silyl groups were observed. Use of the triplet sensitizers (benzophenone, xanthone, and biphenyl) gave only a slight reduction of enantioselectivity in benzylsilane **5**, consistent with triplet isomerization of the exocyclic C=C double bond of silyl-*o*-isotoluene **4**, as described later and predicted by theoretical calculations. Piperylene, a triplet quencher, causes a very limited reduction of the stereoselectivity.

Computational Studies. The mechanism of the photochemical stereoselective reaction of silyl-*o*-isotoluene **4** to benzylsilane **5** (Scheme 3, bottom) was studied with CASSCF, TD-DFT, and DFT computations.[13] We first explored the photochemical [1,3]-shift of a simple model allylic silane, 3-silyl-1-propene. Figure 1 (left) shows the ground state, lowest excited singlet state, and conical intersection (CI) that connects the excited singlet state surface to the ground state surface.

Scheme 4. Proposed Mechanism for the Formation of Silyl-*o*-isotoluene (*R*)-4[a]



[a]The chiral information of the organocatalysts ((*R*)-**3**) is only shown in the stereodetermining step.

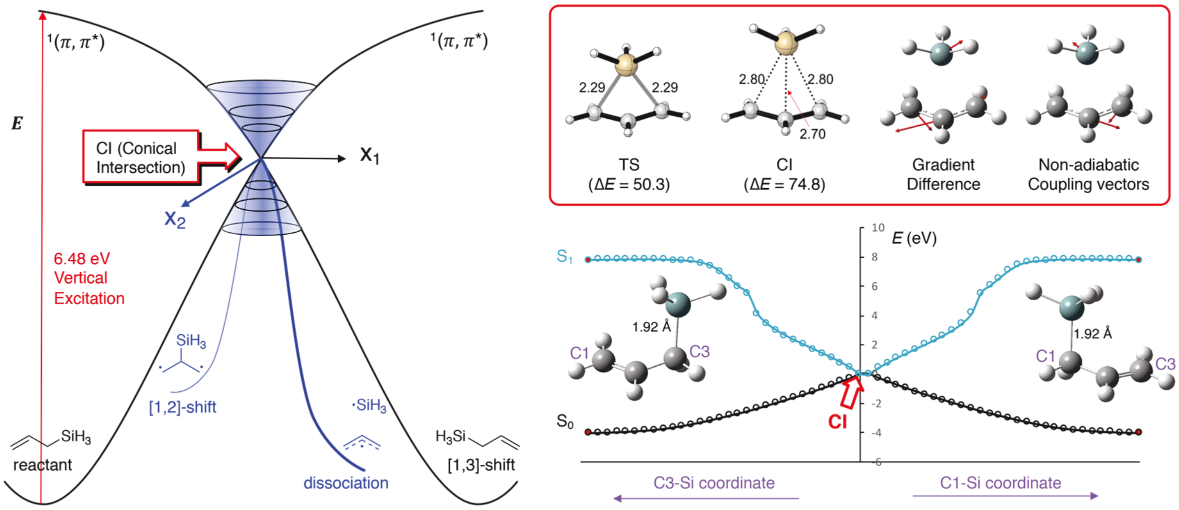


Figure 1. Left: Diagram showing the relationship between the excited state, the conical intersection (CI), and the ground state product of [1r,3s]-sigmatropic shift of 3-silyl-1-propene. The gradient difference vector, $\mathbf{X}_1$, and the nonadiabatic coupling vector, $\mathbf{X}_2$, correspond to the formation of reactant and [1,3]-shift product and indicate how the excited state and ground state degeneracies are lifted to form product. The 1,2-shift and dissociation are less probable. Top-Right: Ground state transition state (TS) calculated by B3LYP/aug-cc-pVTZ//6-31G(d), CPCM ($CHCl_3$, as this is the solvent used in the experimental work), and CI calculated by CASSCF(4,4)/6-31G(d), bond lengths are shown in Å. Single-point electronic energy of CI is 74.8 kcal/mol relative to ground state reactant, calculated by UB3LYP/aug-cc-pVTZ, CPCM ($CHCl_3$). Gradient difference and nonadiabatic coupling vectors of the CI are shown at the top-right of the figure. Bottom-Right: Energy profile produced by steepest gradient descent from CI at the level of CASSCF(4,4)/6-31G(d).

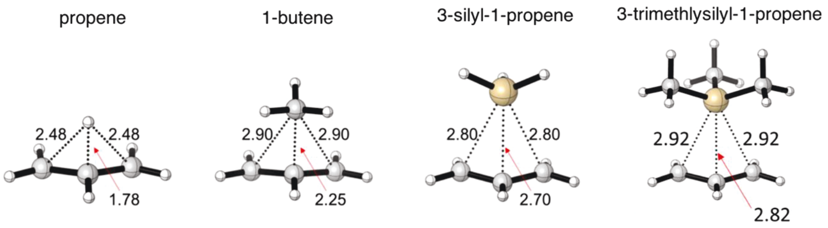


Figure 2. Hydrogen/allyl, methyl/allyl, and silyl/allyl CIs (bond distances are labeled in Å).

Table 1. Computed Values of Electronic Transitions from TD-DFT, M06-2X/aug-cc-pVTZ, CPCM ($CHCl_3$) for (±)-TMS-*o*-isotoluene (Scheme 2b) and Silyl-*o*-isotoluene (*R*)-4 (in Its *Z*-*s*-*cis* Conformation)

(±)-TMS-*o*-isotoluene			(*R*)-*Z*-*s*-*cis*-**4**			
$S_1,\pi-\pi^*$	3.64 eV	341 nm	$S_1,\pi-\pi^*$	3.23 eV	383 nm	375 nm[a]
$S_3,\pi-\pi^*$	5.00 eV	248 nm	$S_6,\pi-\pi^*$	5.23 eV	237 nm	231 nm[a]

[a] Experimentally observed transitions (see Section 7.3 in Supporting Information).

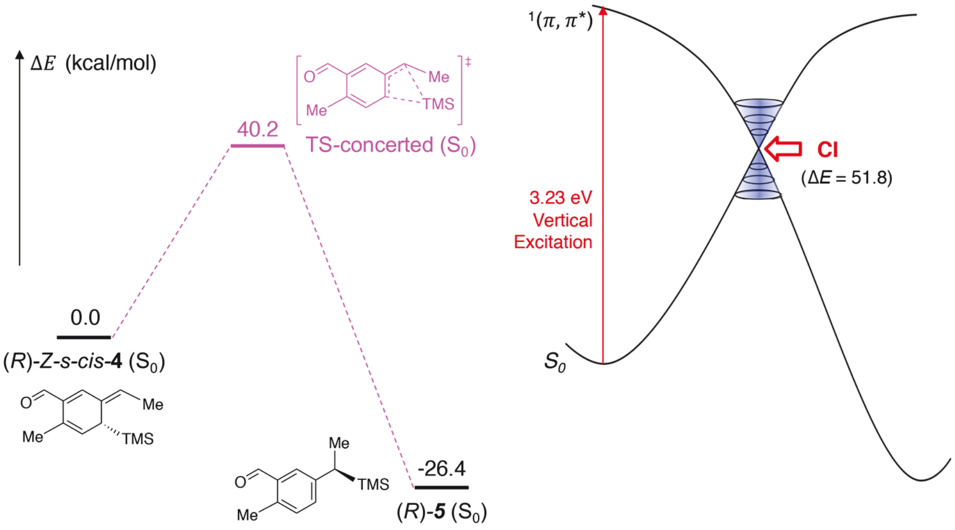


Figure 3. Left: Ground state energetics of (*R*)-*Z*-*s*-*cis*-**4** and the [1,3]-silyl shift to (*R*)-**5**. Electronic energies in kcal/mol, calculated from B3LYP/aug-cc-pVTZ//6-31G(d), CPCM ($CHCl_3$). Right: Diagram showing the relationship between the excited state, CI, and the ground state product of [1,3]-shift of (*R*)-*Z*-*s*-*cis*-**4**. Vertical excitation is calculated from TD-DFT, M06-2X/aug-cc-pVTZ, CPCM ($CHCl_3$); CI is located by CASSCF calculations by choosing a (6,6) active space; single-point electronic energy of CI is calculated with B3LYP/aug-cc-pVTZ, CPCM ($CHCl_3$).

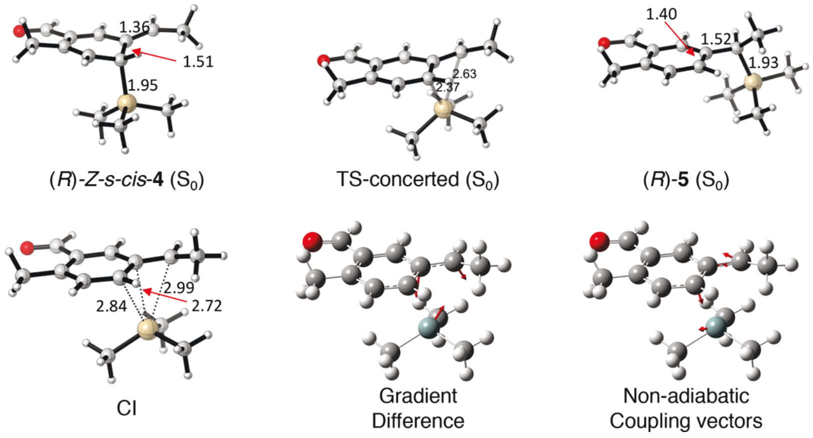


Figure 4. Geometries of stationary points and CI from Figure 3. Bond lengths in Å. Gradient difference and nonadiabatic coupling vectors are shown next to the CI.

A CI is a surface on which the excited state and ground state are degenerate. Internal conversion from the excited state to the ground state through a CI is fully efficient, occurring within one vibrational period.[9] Details on computations of CI are provided in the Supporting Information. The excited singlet state collapses through this CI to the vicinity of the ground transition state for the concerted, thermally forbidden [1r,3s]-shift. The CI was located by complete active space SCF (CASSCF) (4,4) calculations. Figure 2 shows the great similarity of this transition state to those computed earlier for [1,3]-hydrogen and [1,3]-methyl shifts at a somewhat different theory level.[9]

The newly discovered silyl/allyl CI joins the hydrogen/allyl and alkyl/allyl CIs[9] as ubiquitous funnels that connect excited states to ground states. Of particular note are the partial C1−Si and C3−Si bond lengths of 2.80 Å in the silyl/allyl CI, stretched by 0.5 Å relative to the [1,3]-shift transition state as shown in Figure 1.

We also explored computationally the same systems that were studied experimentally. The excited states of (±)-TMS-*o*-isotoluene (Scheme 2b) and silyl-*o*-isotoluene (*R*)-**4** (in its *Z*-*s*-*cis* conformation) (Scheme 3) are summarized in Table 1. The excited states of the two molecules are similar, although the aldehyde functionality in (*R*)-**4** introduces additional higher lying n-π* states. The calculated transitions for (*R*)-**4** are in

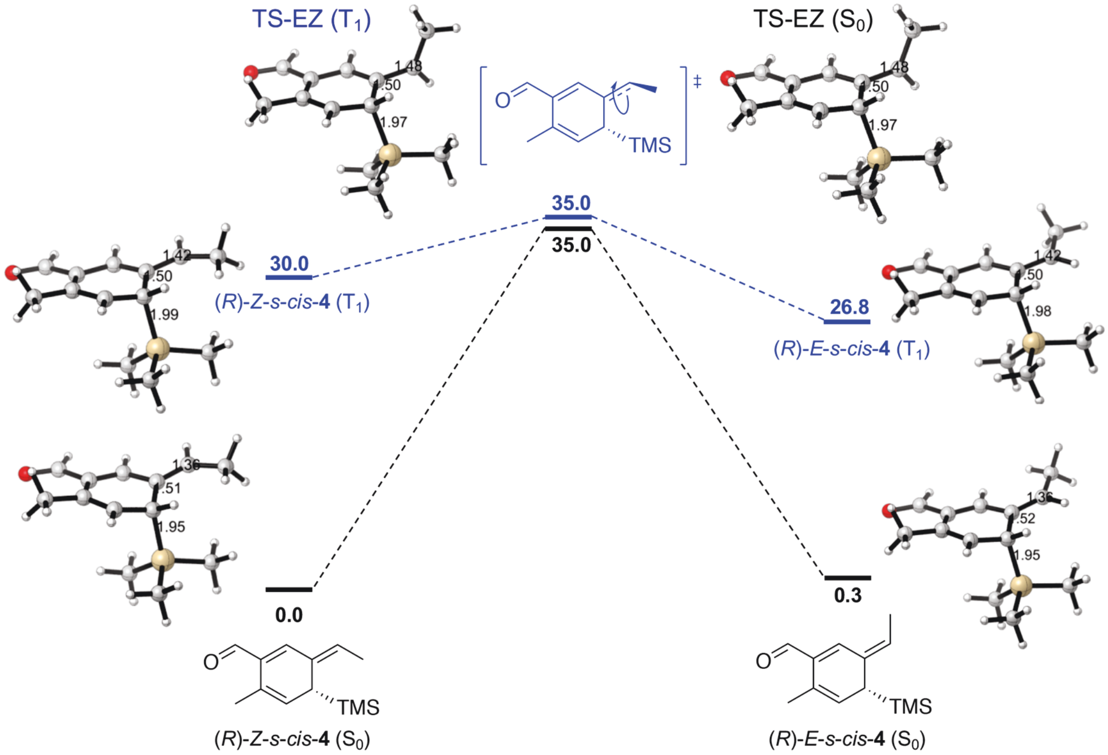


Figure 5. Triplet isomerization surface. Free energies in kcal/mol, calculated from (U)B3LYP/aug-cc-pVTZ//6-31G(d), CPCM ($CHCl_3$); bond lengths are shown in Å.

reasonable agreement with the experimentally observed transitions (see Supporting Information). The lowest excited state is primarily $\pi\pi^*$ with little CT character, but some weakening of the Si−C bond that hyperconjugates with the π system. Kira et al. have studied the excited state properties and reaction of related disilanes and found that a TMS shift involving a Si−Si cleavage can occur via a $\pi\pi^*$ state.[10b]

Figure 3 shows energetics of the [1,3]-silyl shift in the ground state of silyl-*o*-isotoluene **4**, as well as the $^1\pi,\pi^*$ excited state. The vertical excitation is 3.23 eV (383 nm, 74.5 kcal/mol), higher than the CI, which is higher in energy than the ground state transition state.

This CI in Figure 3 then resembles the transition state and leads to the [1,3]-silyl shift product. Figure 4 shows the geometries of various stationary points involved in the photoisomerization.

The sensitized irradiation led to a slightly lower enantiomeric ratio, presumably due to the rotation of the exocyclic double bond in the triplet state. Figure 5 shows the energetics of isomerization on the triplet state surface.

Figure 5 indicates that the rotation from (*R*)-*Z*-*s*-*cis*-**4** (T_1) to (*R*)-*E*-*s*-*cis*-**4** (T_1) requires a transition state energy of 5.0 kcal/mol and may deactivate much more rapidly that rotation. In addition, this triplet state will rarely be formed by intersystem crossing (El-Sayed's rule)[14] from the $^1\pi,\pi^*$ state,[15] and isomerization will then be much less efficient than C−Si partial cleavage to form the CI, and consequently the [1,3]-shift on the singlet surface.

CONCLUSION

We have shown that a novel organocatalytic enantioselective cascade annulation reaction generates a silyl-*o*-isotoluene in high yield and as an enantiopure product (>99:1 e.r.). The silyl-*o*-isotoluene undergoes an unprecedented and highly stereoselective photochemical rearrangement, providing a benzylsilane in 96:4 e.r. Based on a series of experimental and computational studies, the mechanism for the stereoselective silyl/allyl [1,3]-sigmatropic shift has been elucidated. The computational studies show that the [1,3]-sigmatropic shift proceeds by the singlet excited state reaction involving a silyl/allyl conical intersection.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.9b11579.

Experimental procedures, coordinates of all calculated structures, and product characterization data (PDF)

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Notes

The authors declare no competing financial interest.

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