Communication

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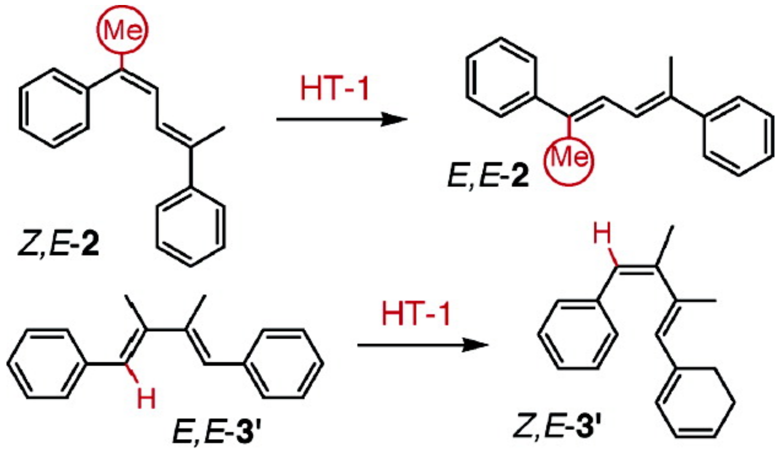

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Steric Effects in Hula-Twist Photoisomerization. 1,4-Dimethyl- and 2,3-Dimethyl-1,4-diphenylbutadienes

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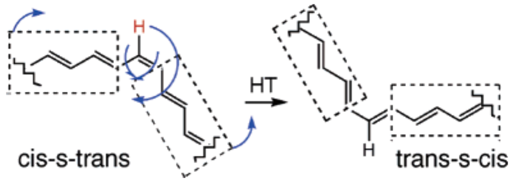
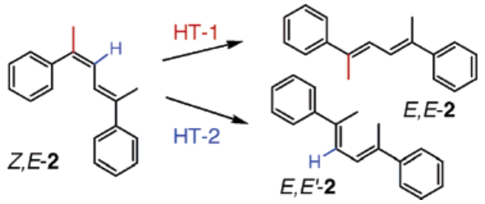
Hula-twist (HT) is a general mechanism of photoisomerization.[1] It is a volume-conserving process of which a single C−H unit moves across the plane of an unsaturated molecule.[2] In contrast, the traditional one-bond-flip (OBF) mechanism turns over one-half of the molecule:



The question whether the process is limited to a small C−H unit has not been answered, although the absence of conformational equilibration of 2,3-dimethyl-1,3-butadiene in argon matrix[3] (in contrast to the parent diene) has been interpreted as steric inhibition due to increased size at the HT reaction center.[1b] However, the work was carried out at a much lower temperature of 10 K (argon matrix); furthermore, the compound simply could have opted for the unhindered HT-1 process, thus leading to no detectable chemical changes. The observed photoisomerization of 1,4-dideutero-2,3-dimethylbutadiene[1b] reflects this possibility. We now report steric effects in HT isomerization of substituted diphenylbutadienes, addressing specifically the issue of possible HT around a C−Me center.

Recently, we reported the HT photoisomerization of isomers of 1,4-diphenyl-1,3-butadiene (DPB), **1**, in EPA glass,[4] demonstrating regioselective HT at center-1 (absence of the central s-cis product expected of HT-2). This selectivity suggested that isomers of 1,4-dimethyl-DPB, **2**, and 2,3-dimethyl-DPB, **3**, will be ideal for probing possible HT around a methyl group. Results of such an investigation are described below.



Irradiation of an EPA (ether:isopentane:ethanol = 5:5:2) solution of either (*E*,*E*)- or (*Z*,*E*)-**2**[5] (200 K) readily produced a photostationary state mixture (Figure 1a,c). The presence of a sharp isosbestic point (especially in the difference spectra, Figure 1b,d) suggests that only the *E*,*E*- and the *Z*,*E*-isomers are present in the mixture (same as the parent DPB).[6] In EPA glass at 77 K, the *E*,*E*-isomer, exhibiting a fine structure in its UV absorption spectrum at 77 K, was unreactive upon irradiation with light >310 nm. This feature is consistent with 1,2-diarylethenes.[4,7]

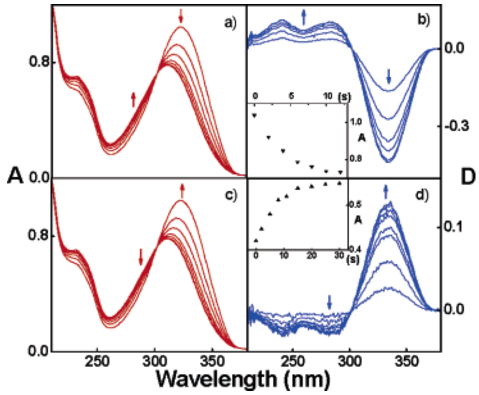


Figure 1. Room temperature irradiation of isomers of **2**. (a) Absorption spectra of (*E*,*E*)-**2** recorded during its irradiation (>310 nm, Corning O-54 filter) in EPA glass at 200 K; $t = 0$, 2, 4, 6, 8, 10, and 12 s. (b) Difference spectra ($t - t_0$) of (*E*,*E*)-**2**. Insert: absorption changes (320 nm) versus time. (c) Absorption spectra of (*Z*,*E*)-**2** recorded during its irradiation (>310 nm, Corning O-54 filter) in EPA glass at 200 K; $t = 0$, 2, 5, 8, 11, 15, 20, 25, and 30 s. (d) Difference spectra of (Z,*E*)-**2**. Insert: absorption changes (333 nm) versus time.

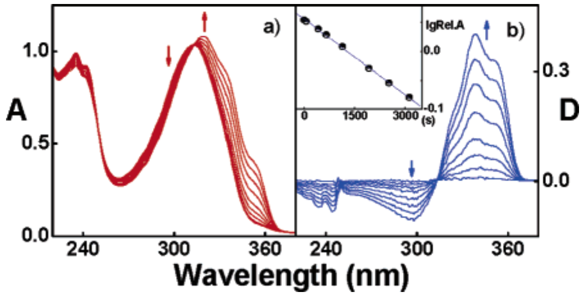


Figure 2. Low temperature irradiation of (*Z*,*E*)-**2**. (a) Absorption spectra of (*Z*,*E*)-**2** recorded during its irradiation (>310 nm, Corning O-54 filter) in EPA glass at 78 K; $t = 0$, 60, 300, 540, 900, 1380, 1920, 2520, and 3120 s. (b) Difference spectra. Insert: log of relative absorbance at 355 nm versus time of irradiation.

Irradiation of (*Z*,*E*)-**2** at 77 K led to a gradual change of the UV absorption spectrum from a broad band to one with a resolved red-shifted absorption band (Figure 2a), suggesting formation of the *E*,*E*-isomer. It was a clean one-to-one conversion, as reflected by the sharp isosbestic point at 313.5 nm. The changes are more clearly revealed in the difference spectra ($t - t_0$) (Figure 2b). Upon thawing the glass medium and recooling to 77 K, the spectrum remained unchanged, thus indicating that a thermally stable photoproduct (the *E*,*E*-isomer) was formed. Hence, same as the parent DPB (**1**),[4] the photoisomerization must have taken place exclusively by way of HT-1, that is, HT around a C−CH_3 unit. After deconvoluting the product spectrum, we found that the irradiated sample contained 18% (*E*,*E*)-**2** and 82% of residual (*Z*,*E*)-**2**.

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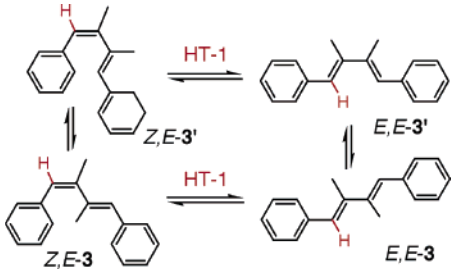
HT involving the C−CH_3 group was, expectedly, much less efficient than that of C−H. The irradiation time needed for the same conversion of (*Z*,*E*)-**2** was approximately 6 times longer than that of the parent (*Z*,*E*)-**1**. However, it is difficult to determine such numbers for solid samples in high precision. Plans are underway to prepare appropriately substituted analogues so as to be able to provide a more manageable internal reactivity ratio between HT-CH_3 and HT-H.



We have also examined photoisomerization of isomers of 2,3-dimethyl-DPB (**3**).[5] The close proximity of the vicinal dimethyl groups presents a different type of steric effect on photochemical properties of the diene. For example, the *E*,*E*-isomer does not exist in the planar form, as suggested by the blue-shifted (λ_{max} 313 nm) UV absorption band at 77 K (Figure 3a). Calculations[8] revealed that (*E*,*E*)-**3** is likely to exist in a twisted (38°) s-trans conformation with a close-lying (1.5 kcal/mol) twisted s-cis conformation in equilibrium. The photoreactivity also reflects the nonplanarity in that the *E*,*E*-isomer is light-sensitive even at 77 K (Figure 3a). A more blue-shifted photoproduct was formed. However, only after warming to room temperature and recooling to 77 K, the UV absorption became identical to that of (*Z*,*E*)-**3**. This photochemical reactivity is unique among all DPBs.

That a conformationally unstable *Z*,*E*-isomer was formed suggests that the reaction originates either from the s-trans form (HT-2) or from the s-cis form (HT-1). We see no easy way to distinguish between the two processes. However, we suspect that the former process involving a hitherto unobserved HT-2 process (especially around a methyl group) is unlikely, and the required s-cis form for HT-1 has been shown to be accessible by calculations.

Irradiation of pure (*Z*,*E*)-**3** led to a more complex change. There was first a facile reaction (<120 s) as reflected in a red-shift and increase in intensity of the UV spectra (insert of Figure 4a), followed by a slow rate of (>160 s) reaction, giving eventually to a more blue-shifted product that exhibited the same fine structures in the high-energy region of the UV absorption spectrum (Figure 4b). The spectra became identical to those of (*E*,*E*)-**3** only after warming up to room temperature and recooling to 77 K. The difference spectra of the *E*,*E*- and *Z*,*E*-isomers revealed that the first stage of photoreaction for the *Z*,*E*-isomer is a mirror image of the reaction for the *E*,*E*-isomer. This suggests that the more twisted isomer (*E*,*E*)-**3′** is the only photoreactive conformer for the *E*,*E*-isomer, which after HT-1 produced (*Z*,*E*)-**3′**, and (*Z*,*E*)-**3′** after HT-1 produced (*E*,*E*)-**3′** with an isosbestic point at 273 nm. Calculations revealed that (Z,*E*)-**3′** likely exists as an s-cis conformer with a close-lying (0.2 kcal/mol) and similarly twisted s-trans conformer, (Z,*E*)-**3**, in equilibrium, and the second stage of photoreaction should be due to the HT-1 of (*Z*,*E*)-**3** giving the stable (*E*,*E*)-**3**. The small spectral changes upon warming and cooling are likely due to changes in the ratio of the conformers that are believed (based on energy calculations)[8] to exist in a ratio close to 1:1 and 10:1 for (*Z*,*E*)-**3** and (*E*,*E*)-**3**, respectively.

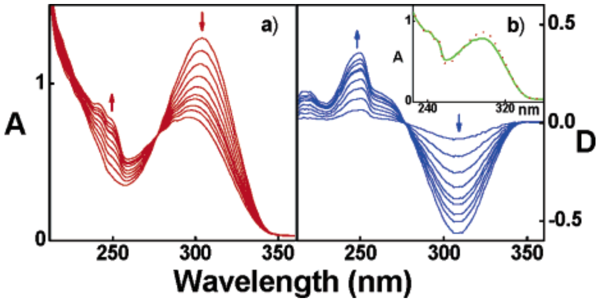


Figure 3. Photoisomerization of (*E*,*E*)-**3**. (a) Absorption spectra of (*E*,*E*)-**3** recorded during its irradiation (>310 nm, Corning O-54 filter) in EPA glass at liquid nitrogen temperature; *t* = 0, 20, 40, 60, 80, 100, 120, 140, 160, and 200 s. (b) Difference spectra. Insert: green solid line, irradiation for 200 s; red dotted line, after warming up to thaw the glass then recooling to low temperature.

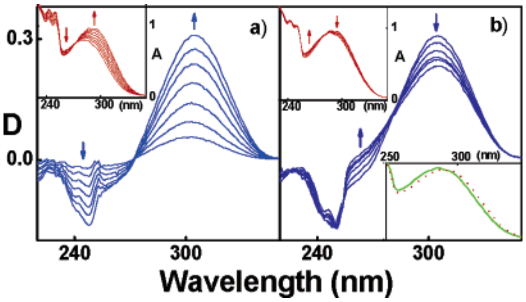


Figure 4. Photoreaction of (*Z*,*E*)-**3** at low temperature. Insert a, left top: absorption spectra recorded during the earlier stage of its irradiation (>310 nm, Corning O-54 filter) in EPA glass at 78 K; *t* = 4, 8, 15, 25, 40, 60, and 120 s. (a) Difference spectra ($t - t_0$) during the early stage. Insert b, left top: absorption spectra recorded during the second stage of its irradiation under the same condition; *t* = 160, 200, 240, 280, 320, and 400 s. (b) Difference spectra in the late stage. Insert, right bottom: green solid line, after irradiation for 400 s; red dotted line, after warming up to thaw the glass then recooling to low temperature.

In summary, both 1,4- and 2,3-methyl substituents played significant roles on the photoreactivity of DPBs. While regiospecific HT-1 photoisomerization is retained for 1,4-dimethyl-DPB, it proceeded by way of the unprecedented HT-Me within the confined cavity of amorphous organic glass. The nonplanar 2,3-dimethyl-DPB introduced unexpected reactivity. Even the *E*,*E*-isomer undergoes regiospecific HT-1 isomerization.[9]

Acknowledgment. The work was supported by grants from Hawaii NSF-EPSCoR (CHE-01-32250) and Kentucky NSF-EPS-CoR (4-65752-03-397).

Supporting Information Available: NMR and UV data of isomers of **2** and **3**, and complete ref 8. This material is available free of charge via the Internet at http://pubs.acs.org.

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(9) Note added after acceptance of this paper. A recent article (*J. Am. Chem. Soc*. **2005**, *127*, 6938−6939) claimed the absence of HT in their study of 1-(2-naphthyl)-2-phenylethylene. Unfortunately, the authors overlooked the simple fact of the presence of two different HT processes in their compound, which in fact is not expected to provide distinguishable data between HT and OBF processes.

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