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One-Way Photoisomerization of Dienes Substituted by an Anthracene Nucleus

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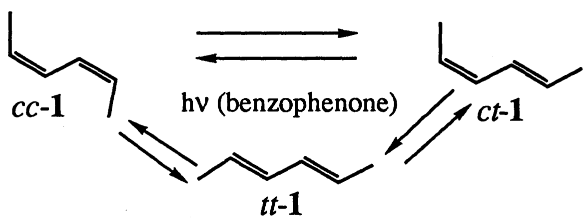
On benzil sensitization, 1-(2-anthryl)-1-*cis*,3-*trans*-pentadiene and *cis*-1-(2-anthryl)-4-methyl-1,3-pentadiene underwent one-way cis→trans isomerization with high quantum efficiencies in an adiabatic process at the excited triplet state.

Stilbene undergoes mutual isomerization between the cis and trans isomers at the triplet state with quantum yields of ca. 0.5 for both directions.[1)] 2,4-Hexadiene (**1**) undergoes mutual photoisomerization among the isomers, but the isomerization proceeds through quantum chain processes not only from cis to trans isomers, but also from trans to cis isomers.[2)]



Recently, we have found that substitution of an aromatic nucleus with a low triplet excitation energy like anthracene on an ethylenyl carbon leads to photochemical cis→trans one-way isomerization of the double bond proceeding at the triplet state with a quantum chain process in being contrast to the well studied mutual isomerization between the cis and trans isomers of stilbenes.[3-6)] However, till now the effect of aromatic substituents on the isomerization of dienes in the excited triplet state has scarcely been reported.[7,8)] In this respect, we are prompted to examine the effect of replacement of a methyl group of **1** by an aromatic nucleus with a low triplet excitation energy like anthracene to reveal whether it changes the mode of the isomerization of the diene from mutual isomerization with quantum chain processes to one-way cis-to-trans isomerization with a quantum chain process of higher efficiency or does not. We now report that 1-(2-anthryl)-1-*cis*,3-*trans*-pentadiene (abbreviated as *ct*-**2**) and *cis*-1-(2-anthryl)-4-methyl-1,3-pentadiene (*cis*-**3**) undergo photochemical one-way isomerization of their cis double bond to trans double bond in the triplet manifold with very high quantum efficiencies.

The dienes, *ct*- and *tt*-**2** and *cis*- and *trans*-**3**, were synthesized by the Wittig reaction of the ylide prepared from (2-anthrylmethyl)triphenylphosphonium bromide with *trans*-2-butenal and 3-methyl-2-butenal, respectively, as mixtures of cis and trans isomers around the double bond adjacent to the anthracene nucleus. The cis and trans isomers were carefully separated by flash column chromatography with hexane as an eluent under red light, and then further purified by recrystallization from cyclohexane or heptane. The structure was determined by NMR and mass spectroscopy, and elemental analysis.[9)]

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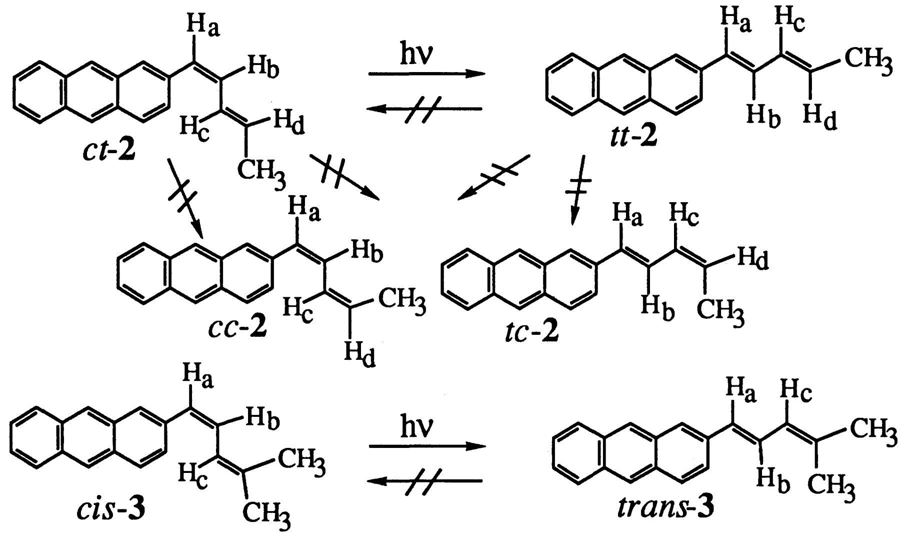

On benzil (0.01 M, 1M=1 mol dm^{-3}) (the triplet energy, E_T=53.4 kcal mol^{-1}, 1 cal=4.184 J)[10] sensitization at 435 nm in benzene *ct*-**2** and *cis*-**3** isomerized solely to *tt*-**2** and *trans*-**3**, respectively, while no reverse isomerization took place from trans to cis isomers as determined by HPLC analysis. None of *cc*-**2** and *tc*-**2** were produced on benzil sensitization of *ct*-**2** or *tt*-**2**. The quantum yields of benzil-sensitized isomerization from *ct*- to *tt*-**2** ($\Phi_{ct\rightarrow tt}$) and *cis*- to *trans*-**3** ($\Phi_{c\rightarrow t}$) increased with concentration of cis isomer to attain as high as 24 and 11 at 5×10^{-3} M of *ct*-**2** and 2×10^{-3} M of *cis*-**3**, respectively (Fig. 1).

Excitation of both *ct*- and *tt*-**2** with a 435 nm dye laser (Stilbene 3, 10-ns fwhm) afforded essentially the same transient absorptions as shown in Fig. 2 (λ_{max}(T-T): 450 and 610 nm) decaying with a lifetime of 8μs under argon atmosphere. Both of these transients were quenched by molecular oxygen in a rate constant of 3×10^9 M^{-1} s^{-1} and, therefore, are reasonably assigned to the trans triplet state (^{3}*tt*-**2***) not to the perpendicular triplet.[11] Both of these transients were also quenched by azulene (E_T=39.8 kcal mol^{-1}) with rate constants (ca. 10^9 M^{-1} s^{-1}) slightly less than the diffusion controlled rate constant. Thus, the triplet energy of ^{3}*tt*-**2*** over the trans ground state is estimated as ca. 39 kcal mol^{-1}. The diene **3** exhibits T-T absoption (lifetime: 7μs) which is quenched by oxygen and azulene with similar rate constants as **2** and is reasonably assigned to ^{3}*trans*-**3***.

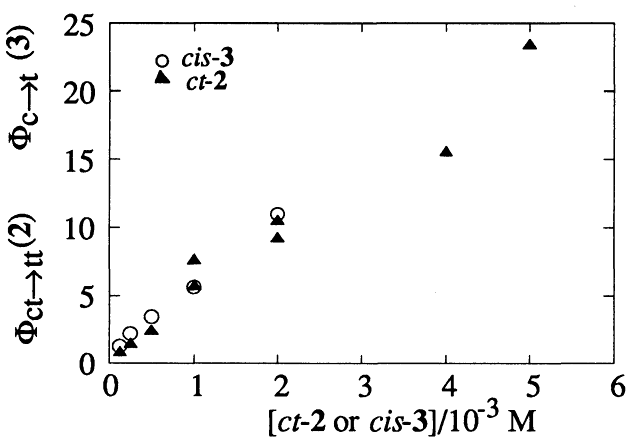

Fig. 1. Quantum yields of cis →trans isomerization of *ct*-**2** and *cis*-**3** on benzil sensitization under argon at room temperature.

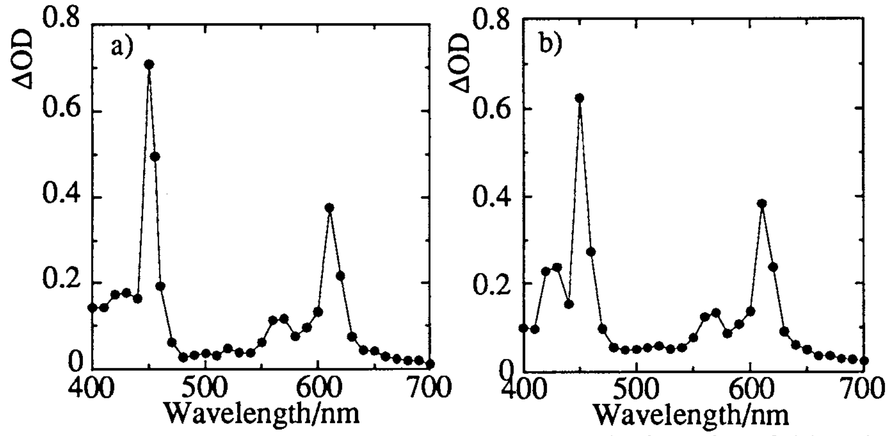

Fig. 2. T-T Absorption spectra observed on excitation of *ct*-**2** (a) and *tt*-**2** (b) in benzene at room temperature.

Observation of the highly efficient quantum chain isomerization as well as the assignment of the observed triplet state to stable ^3tt-**2*** and ^3trans-**3*** clearly indicate that **2** and **3** undergo one-way cis→trans isomerization at the triplet state by an adiabatic process followed by energy transfer from the resulting ^3tt-**2*** or ^3trans-**3*** to *ct*-**2** or *cis*-**3** to regenerate ^3ct-**2*** or ^3cis-**3***, respectively. Scheme 1 depicts the triplet sensitized reaction mechanism for **2**,[12] where S denotes the triplet sensitizer, benzil, and the superscript 3 means the triplet excited state.

$$^3S^* + ct\text{-}2 \xrightarrow{\Phi(^3ct\text{-}2^*)} S + {}^3ct\text{-}2^* \quad (1)$$

$$^3ct\text{-}2^* \longrightarrow {}^3tt\text{-}2^* \quad (2)$$

$$^3tt\text{-}2^* \xrightarrow{1/\tau_T} tt\text{-}2 \quad (3)$$

$$^3tt\text{-}2^* + ct\text{-}2 \xrightarrow{kq} tt\text{-}2 + {}^3ct\text{-}2^* \quad (4)$$

Scheme 1.

$$\Phi_{ct\rightarrow tt} = \Phi_{isc}\,\Phi(^3ct\text{-}2^*)(1+k_q\tau_T[ct\text{-}2]) \quad (5)$$

The quantum yield of the benzil-sensitized isomerization of *ct*-**2** is expressed by eq. 5, where, Φ_{isc}, $\Phi(^3ct\text{-}2^*)$, k_q, and τ_T are the quantum yield of intersystem crossing from the singlet to the triplet excited state of benzil (=0.92),[10] the efficiency of energy transfer from the benzil triplet to *ct*-**2**, the rate constant of energy transfer from ^3tt-**2*** to *ct*-**2** to regenerate ^3ct-**2***, and the lifetime of ^3tt-**2***, respectively. One can estimate k_q from the slope in Fig. 1; in the condition of Fig. 1, $\Phi(^3ct\text{-}2^*) \approx 1$, therefore, $k_q\tau_T$ value for **2** is obtained as 4.5×10^3 M^{-1}. With τ_T=8 μs under argon atmosphere, kq is estimated as ca. 6×10^8 M^{-1} s^{-1}, nearly 1/15 of the diffusion controlled rate constant in benzene, which means that the energy transfer from ^3tt-**2*** to *ct*-**2** is slightly endoergonic.

The present results of **2** and **3** are very much contrasted to the behavior of 1,3-pentadiene and **1**.[2)] **1** undergoes isomerization mutually among cc, ct, and tt isomers with quantum chain processes for tt→ct, tt→cc, cc→tt, and cc→ct. For example, the quantum yields of isomerization from *cc*-**1** to *ct*-**1** and *tt*-**1** to *ct*-**1**, $\Phi_{cc\rightarrow ct}$ and $\Phi_{tt\rightarrow ct}$, increased from 0.82 and 0.59 to 1.80 and 1.05, respectively, with increasing the initial *cc*-**1** and *tt*-**1** concentration from 1.74 to 7.83 M.[2a)] The occurence of the quantum chain isomerization indicates that in the excited triplet state of **1** the energy minimum must be situated at cc, ct, and tt conformers as well as at the twisted triplet state, which causes the unimolecular deactivation from the twisted triplet state and the bimolecular deactivation from cc, ct, and tt accompanied by the energy transfer to the starting isomer.

In the present work, substitution of an anthracene nucleus on diene afforded $\Phi_{ct\rightarrow tt}$ of **2** as high as more than 20 at much lower concentration than **1** ([*ct*-**2**]=5×10^{-3} M), not accompanied at all by isomerization from *tt*-**2** to any cis isomers (*ct*-, *tc*-, and *cc*-**2**).

Therefore, substitution of an anthracene nucleus on diene can control the mode of the isomerization leading to highly specific isomerization of very large quantum efficiency by completely suppressing the quantum chain isomerization from trans to cis double bond observed in **1**.

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9) ^{1}H NMR data in $CDCl_3$: *ct*-**2**; δ 1.84 (3H, CH_3, dq, J=6.8, 2.6 Hz), 5.95 (1H, H_d, dq, J=15.0, 6.8 Hz), 6.31 (1H, H_b, dd, J=11.4, 11.6 Hz), 6.46 (1H, H_a, d, J=11.6 Hz), 6.76 (1H, H_c, ddq, J=11.4, 15.0, 2.6 Hz), 7.45 (3H, m), 7.97 (4H, m), 8.38 (1H, s), 8.39 (1H, s). *tt*-**2**; δ 1.87 (3H, CH_3, d, J=7.6 Hz), 5.90 (1H, H_d, dq, J=7.6, 15.0 Hz), 6.30 (1H, H_c, dd, J=10.7, 15.0 Hz), 6.64 (1H, H_a, d, J=15.7 Hz), 6.90 (1H, H_b, dd, J=10.4, 15.7 Hz), 7.61 (3H, m), 7.94 (4H, m), 8.33 (2H, s). *cis*-**3**; δ 1.87 (3H, s), 1.89 (3H, s), 6.46-6.60 (3H, m), 7.41-7.49 (3H, m), 7.93-8.00 (4H, m), 8.37 (1H, s), 8.38 (1H, s). *trans*-**3**; δ 1.89 (3H, s), 1.92 (3H, s), 6.09 (1H, H_c, d, J=10.9 Hz), 6.64 (1H, H_a, d, J=15.5 Hz), 7.14 (1H, H_b, dd, J=10.9, 15.5 Hz), 7.42-7.46 (2H, m), 7.66 (1H, d, J=8.9 Hz), 7.82 (1H, s), 7.91-7.97 (3H, m), 8.33 (2H, s).

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12) For **3**, *ct*-**2** and *tt*-**2** in Scheme 1 are replaced by *cis*-**3** and *trans*-**3**, respectively.

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