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Cycloreversion of 1,4-Diphenylbicyclo[3.2.0]hept-2-ene via Triplet State. Evidence for Adiabatic Process on the Triplet Surface

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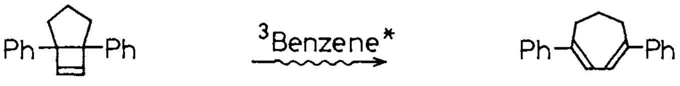
The cycloreversion of 1,4-diphenylbicyclo[3.2.0]hept-2-ene (**1**) under triplet sensitization in benzene has been studied by γ-radiolysis and pulse radiolysis. It has been found that the cycloreversion of **1** to 1,4-diphenyl-1,3-cycloheptadiene proceeds by an adiabatic mechanism.

The cycloreversion of cyclobutene and the related compound by pyrolysis and photoexcitation is one of the most fundamental organic reaction. Therefore the cycloreversion has been extensively investigated by pyrolysis and photoreaction involving electron donor-acceptor system.1) However, little is known about the cycloreversion of cyclobutene compounds via the triplet state, since they have too high triplet energy to allow the sensitization by such typical triplet-sensitizers as benzophenone (BP). We have developed the triplet reaction sensitized by the triplet state of benzene generated by γ-radiolysis and pulse radiolysis.2) Here we report on the cycloreversion of 1,4-diphenylbicyclo[3.2.0]hept-2-ene (**1**) to 1,4-diphenyl-1,3-cycloheptadiene (**2**)3) via triplet state by γ-radiolysis and pulse radiolysis.



1 2

The γ-radiolysis of **1** (0.01 mol dm^{-3}) in benzene gave **2** quantitatively up to a stationary state where the ratio of **1** to **2** is 0 : 100 whereas no isomerization from **2** to **1** occurred (Fig. 1).[4] The triplet energy of **1** was estimated to be 78 kcal mol^{-1} from 0-0 band (369 nm) of its phosphorescence spectrum measured in an EPA solution at 77 K (Fig. 2).[5] Triplet state of benzene can be generated by γ-radiolysis of benzene (G = 4.7).[6] Since the triplet state of benzene has relatively high energy (84.3 kcal mol^{-1}),[7] γ-radiolysis of a benzene solution is a very useful method to produce the triplet state of the solute added in benzene. The participation of the ionic species from **1** can be ruled out by the fact that the formation of **2** was not affected by the addition of ion scavenger such as n-buthylchloride.

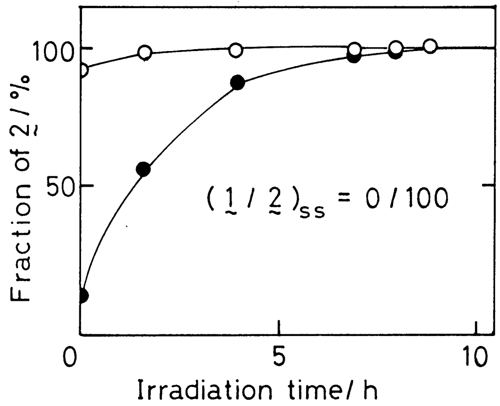


Fig.1. The γ-radiolysis of **1**(●) and **2**(○) in benzene ; [1]=[2]= 4 mmol dm^{-3} .

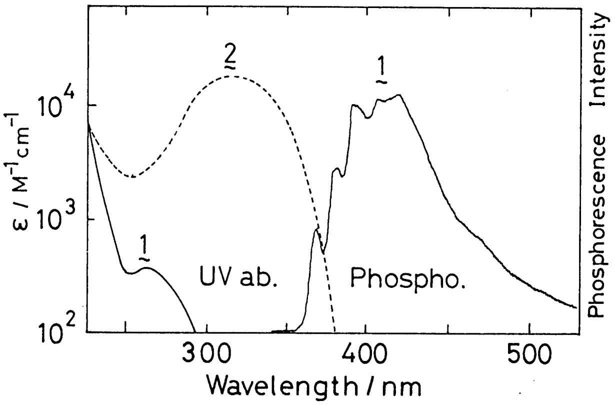


Fig.2. UV absorption spectra of **1** and **2** in hexane at room temperature and phosphorescence spectrum of **1** in an EPA solution at 77 K.

For the mechanistic analysis, T-T absorption spectra were measured by a nanosecond pulse radiolysis for the degassed benzene solution.[8] In the case of **1**, the absorption maxima are observed at 325 nm and 380 nm (Fig.3). The transient absorption at 380 nm raised immediately after irradiation and then decayed at a rate of 3.6×10^5 s^{-1}. A transient absorption band at 325 nm decayed rapidly and then gradually raised. The slow formation was assigned to **2** in ground state since the band agreed with the UV absorption spectra of **2** shown in Fig. 2 and was not affected by the addition of oxygen. The absorption of triplet state of **1** was not observed in transient absorption spectra of **1** in Fig.3.

In the case of **2**, the transient species measured immediately after the pulse had a λ_{max} around 385 nm. This band decayed in first order with a decay constant of 3.8×10^5 s^{-1} . In order to conform the formation of the triplet **2**, the pulse radiolysis of **2** was carried out in the presence of BP

(E_T = 69 kcal mol^{-1}). The T-T absorption band of BP (λ_{max} 530 nm) decayed rapidly and the simultaneous formation of a new absorption band due to substrate was observed (Fig. 4). An ε_{max} value of triplet **2** was estimated to be 3.0 x 10^5 dm^2 mol^{-1} by means of the ε_{max} value of triplet BP.[9)]

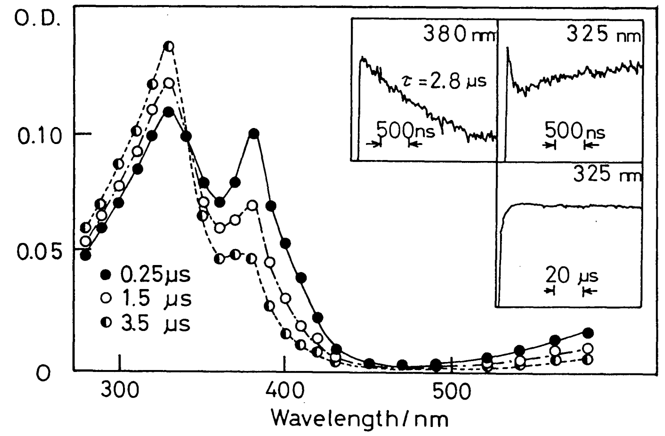


Fig.3. T-T absorption spectra of **1** in benzene; [**1**]= 4 mmol dm^{-3}.

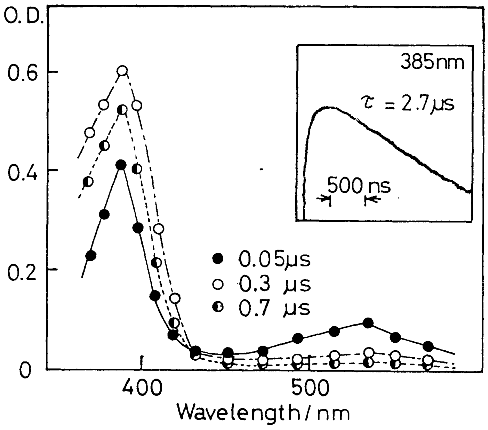
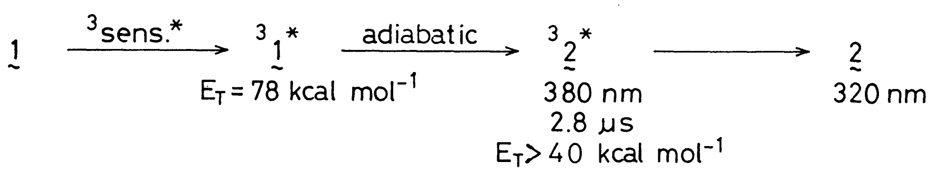


Fig.4. T-T absorption spectra of **2** in the presence of BP in benzene; [**2**]= 4 mmol dm^{-3} and [BP]= 20 mmol dm^{-3}.

Spectral features of the transient species observed for **1** and **2** are summarized as follows. A common intermediate (λ_{max} 380-385 nm, τ = 2.7-2.8 µs) was observed in both compounds **1** and **2** ,which was assigned to a triplet state with a structure of **2**, on the basis of the following observations: (i) The 380-385 nm band of this species is very close to that of 1,4-diphenyl-1,3-butadiene[10)] (**3**; λ_{max} = 390 nm) and its lifetime is long (µs order) and (ii) The 380-385 nm band is quenched not only by oxygen (**1**; 1.8 x 10^9 dm^3 $mol^{-1}s^{-1}$, **2**; 1.7 x 10^9 dm^3 $mol^{-1}s^{-1}$) but also by azulene (E_T = 39.8 kcal mol^{-1})[11)](**1**; 5.8 x 10^8 dm^3 $mol^{-1}s^{-1}$, **2**; 4.9 x 10^8 dm^3 $mol^{-1}s^{-1}$). From this experiment, we assume that the triplet energy of **2** is more than 40 kcal mol^{-1}. Since the conversion of **1** into **2** is exothermic process of ca. 58 kcal mol^{-1} which was calculated using E_T values and the strain energy difference (20 kcal mol^{-1}) between **1** and **2**.[12)] The participation of other intermediates such as 1,4-biradical would be ruled out. Therefore, it is suggested that the triplet state of **1** is readily converted into the triplet state of **2** by an adiabatic process along down hill energy surface (Scheme 1).



Scheme 1.

References

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2) T. Kitamura, S. Toki, S. Takamuku, and H. Sakurai, Chem. Lett., **1980**, 145; K. Nakabayashi, S. Toki, and S. Takamuku, Chem. Lett., **1986**, 1889 ; H. Nishino, S. Toki, and S. Takamuku, J. Am. Chem. Soc., **108**, 5030 (1986); K Nakabayashi, H. Nishino, S. Toki, and S. Takamuku, Radiat. Phys. Chem., **34**, 809 (1989).

3) Compounds **1** and **2** were synthesized by a literature procedure; P. Courtot, Ann. Chem., **8**, 197 (1963).

4) γ-Radiolysis in benzene was carried out in pyrex cells using a ^{60}Co source up to a dose of 0.49 kGy at room temperature. The products were determined by HPLC. The 100 eV yield for the isomerization of **1** to **2** was 3.5.

5) The spectra were measured in deaerated EPA (ether:isopentane:ethanol = 5:5:2) on Shimadzu RF-501 spectrophotometer equipped with phosphorescence accessories.

6) R. B. Cundall and W. Tippett, " Radiation Chemistry, Vol II, in Advances in Chemistry Series, 82," Am. Chem. Soc., Washignton D.C., (1968), p387.

7) S. M. Murov, "Handbook of Photochemistry," Marcel Decker, New York, (1973), p19.

8) The L-band linear accelerator at Osaka University (pulse width: 8 ns) was used as the source of electron pulse. The energy was 28 MeV and the dose was 0.74 kGy per pulse. A 450 W xenon pulse lamp (OPG-450, Osram), a monochrometer (Nikon, G-250), a photomultiplier (R-928), and a programmable digitizer (Tektronix 7912AD) were used for the observation of transient spectra.

9) R. Bensasson and E. J. Land, Trans. Faraday Soc., **67**, 1904 (1971).

10) Compound **3** was used as model compound of **2**. The λ_{max} of transient spectra was 390 nm and the triplet lifetime was 1.9 μs in benzene.

11) A. A. Gorman, I. Hamblett, M. Irvine, P. Raby, M. C. Standen, and S. Yeates, J. Am. Chem. Soc., **107**, 4404 (1985).

12) The value was obtained by a Seiko Electric DSC-200/SSC5000 at the Laboratory of Research Institute for Polymers and Textiles.

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