CHEMISTRY LETTERS, pp. 1447-1450, 1993. © 1993 The Chemical Society of Japan

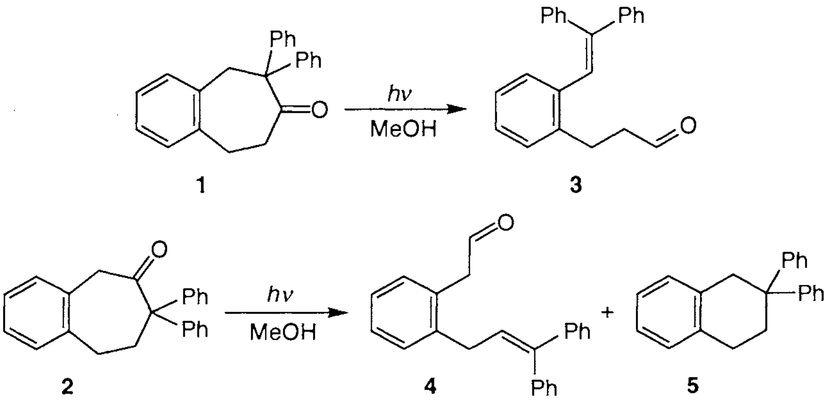
Norrish Type I Reaction of Diphenyltetrahydrobenzocycloheptenones. Conformational Effects on Biradical Lifetime

Ryoko TANAKA, Yasunao KURIYAMA, Hiroki ITOH,[†] Hirochika SAKURAGI,* and Katsumi TOKUMARU
Department of Chemistry, University of Tsukuba, Tsukuba, Ibaraki 305
† Department of Chemistry, Faculty of Science, Yamagata University, Koshirakawa, Yamagata 920

Isomeric 6,6-diphenyl-6,7,8,9-tetrahydro-5*H*-benzocyclohepten-7-one and 7,7-diphenyl-6,7,8,9-tetrahydro-5*H*-benzocyclohepten-6-one (**2**) were photolyzed in methanol to give rise to unsaturated aldehydes as well as diphenyltetrahydronaphthalene, a decarbonylation product (for **2**). Lifetimes of the intermediate triplet biradicals were dependent on their structures, indicating that cyclic conformations play an important role in the intersystem crossing of biradicals.

In a previous communication[1)] we reported that the reaction course of biradicals, $O{=}C^{\uparrow}\text{-}(CH_2)_{n-2}\text{-}C^{\uparrow}Ph_2$, generated from Norrish type I reaction of 2,2-diphenylcycloalkanones with various ring sizes, is switched from intramolecular disproportionation (n = 6 and 7) to acyl-phenyl recombination (n = 9, 11, 12, and 13) and that the intersystem crossing of the triplet biradicals takes place in their cyclic conformations favorable for giving cyclization or disproportionation products in the singlet biradicals.

Introduction of conformational constraints in biradical skeleton can control distance between the termini and orbital orientation of the radical centers, and sometimes provide informations of conformational dependence of their intersystem crossing.[2–4)] We have prepared diphenyltetrahydrobenzocycloheptenones, **1** and **2**, and investigated their photochemical behavior. The Type I reaction of these substrates gives acyl-diphenylmethyl biradicals with limited chain movement and, therefore, with significantly different lifetimes by a benzene ring incorporated in the molecular frame. We wish to describe conformational effects on biradical behavior in these systems.

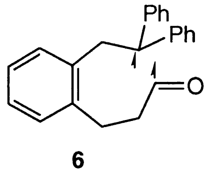


Scheme 1.

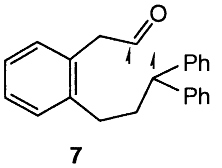
Irradiation of **1** with 313-nm light in methanol gave exclusively an unsaturated aldehyde (**3**) in 95% yield; however, similar irradiation of **2** afforded an unsaturated aldehyde (**4**) and a tetrahydronaphthalene (**5**) in 47 and 40% yields, respectively.[5)] The quantum yields for disappearance of **1** and **2** were nearly 0.3.[6)] The formation of the unsaturated aldehydes suggests Norrish Type I cleavages of triplet ketones followed by 1,6-hydrogen shift of intermediate acyl-diphenylmethyl biradicals (**6** and **7**), as previously reported for 2,2-diphenylcycloheptanone.[1)] Tetrahydronaphthalene **5** is a cyclization product of decarbonylated biradicals (**8**) from **2**.

Pulsed laser excitation of **1** and **2** exhibited transient absorption spectra ascribable to Norrish I biradicals **6** and **7**, and decarbonylated biradicals **8**. Figures 1 and 2 depict the transient absorption spectra observed for **1** and **2**, respectively.[8)] The absorption bands with a maximum around 335 nm are characteristic of a diphenylmethyl radical terminus and can be ascribed to triplet biradicals with such a terminus.[1)] The absorption spectrum observed at 391 ns after laser excitation of **1** is ascribed to the product. The decay profile of transient absorption monitored at 337 nm for **1** fits a single-exponential decay with a lifetime of 93 ns, while that for **2** fits a double-exponential decay with lifetimes of 48 and 890 ns. The lifetimes of 93 and 48 ns are comparable with, and shorter than, that (97 ns) of the Norrish I biradical from 2,2-diphenylcycloheptanone,[1)] and that of the longer-lived component from **2** is close to the lifetime (920 ns) of $\mathrm{PhCH^{\uparrow}\text{-}(CH_2)_4\text{-}CH^{\uparrow}\text{-}Ph}$.[10)] The great difference in lifetime arises from a difference in intersystem crossing mechanism,[11)] the spin-orbit interaction for **6** and **7**, and the hyperfine interaction for **8**.

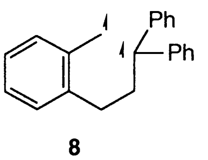
Biradical **8** could be formed by way of decarbonylation of Norrish I biradicals **7** or **9**. In order to clarify the pathway of **8** formation and the decay process of the biradicals we measured temperature dependence of biradical lifetimes in methanol.[12)] Figure 3 shows Arrhenius plots of decay for biradicals **6**, **7**, and **8**, and Table 1 summarizes the resulting activation parameters. The extremely small activation energies for **6** and **7** as well as **8** indicate that their decay rates correspond to the intersystem crossing[13),14)] but not to decarbonylation, in which much higher values might be involved such as 29 kJ mol^{-1} for $\mathrm{PhCH_2CO\cdot}$.[15)] These observations indicate that **8** is generated from rapid decarbonylation of **2** triplets probably through **9**, and that decarbonylation of **7** is unde-



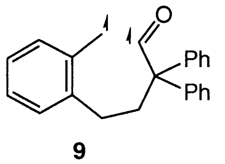
6



7



8



9

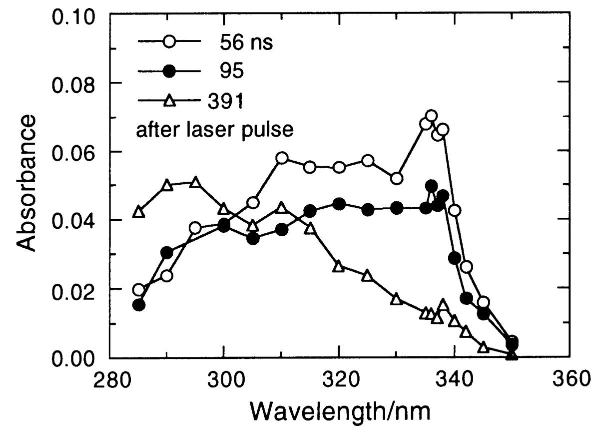


Fig. 1. Transient absorption spectra observed on 308-nm pulsed laser excitation of **1** in methanol.

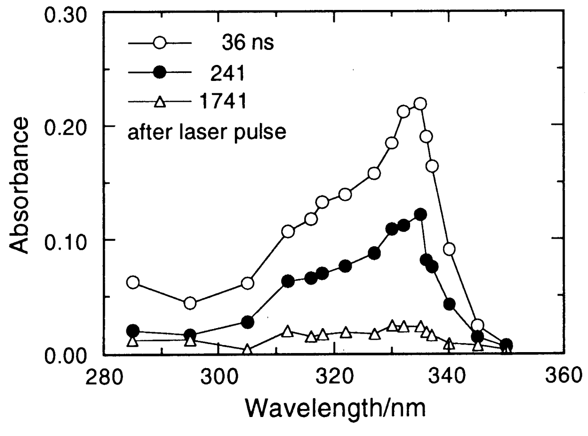
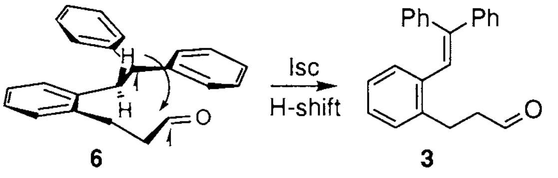


Fig. 2. Transient absorption spectra observed on 308-nm pulsed laser excitation of **2** in methanol.

Table 1. Activation Parameters for Decay of Biradicals **6**, **7**, and **8** in methanol

Biradical	E_a/kJ mol^{-1}	log (A/s^{-1})
6	5.4	7.9
7	6.3	8.4
8	0.46	6.2



Scheme 2.

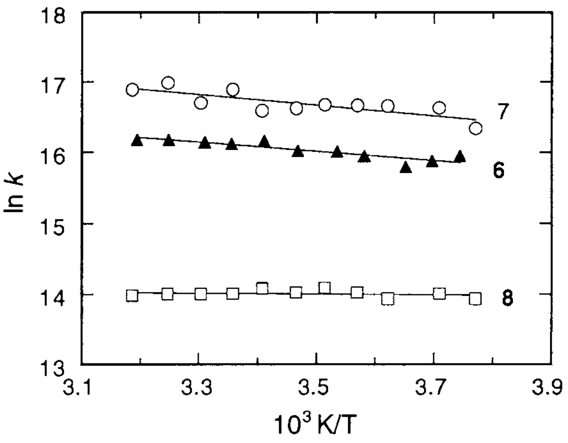
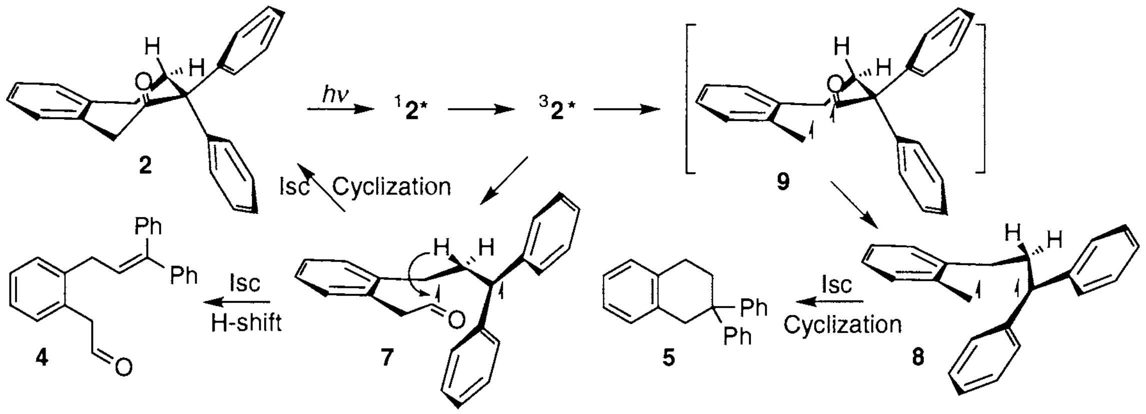


Fig. 3. Arrhenius plots of decay for biradicals **6**, **7**, and **8**.



Scheme 3.

tectably slow even though it gives a benzylic radical terminus. This is supported by observations that the quantum yield for **5** formation (0.13) was very similar to that for **8** formation (ca. 0.1) (*vide infra*) and that the Type I reaction of **2** gave a lower yield (31%) of aldehyde **4** in carbon tetrachloride than in methanol though **5** was formed in almost the same yields in both solvents. Biradical **7**, the precursor of **4**, may be trapped by the solvent carbon tetrachloride.[16,17]

More remarkable is the difference in lifetime between biradicals **6** and **7**. A factor of two is a big difference for these structurally similar biradicals, since the lifetimes of a series of biradicals with varying chain lengths, $O{=}C^{\dagger}\text{-}(CH_2)_{n-2}\text{-}C^{\dagger}Ph_2$ (n = 6-13), are among 67–120 ns in methanol.[18,19] Also, it is reported that the aromatic ring in the molecular frame connecting the radical centers shows little effects on the lifetime of non-benzylic biradicals.[4] The quantum yields for **6** and **7**+**8** formation are nearly 0.2 and 0.4 (ca. 2:1 for **7**:**8**), respectively, at room temperature in methanol, as evaluated from their absorption intensities immediately after pulsed laser excitation of the ketones.[20] These values can be taken as almost the same as the quantum yields for disappearance of the starting ketones, indicating that the main pathway for collapse of the biradicals is the product formation. Consequently, the difference in biradical lifetime could be ascribed to conformational factors affecting intersystem crossing.

The chain motions of biradicals **6** and **7** are much limited due to the presence of the benzene ring in the molecular frame. For efficient hydrogen shift the corresponding singlet biradicals need to take a conformation in which the singularly occupied *p* orbital at the diphenylmethyl moiety overlaps with the C-H bond to be broken. Such a conformation may be more constrained in **6** than in **7**, since one of the phenyl groups of the diphenylmethyl moiety of **6** is located at the closer position to the benzene ring in the molecular frame than does that of **7**, as can been seen from Dreiding models, and therefore, the particular conformation can be attained more easily in **7** than in **6** (Schemes 2 and 3). Such structural features that make the hydrogen shift slow might then extend the biradical lifetime. These results are consistent with our previous results1) and with the concept that the intersystem crossing in triplet biradicals takes place in the conformations that are favorable for product formation.23)

References

1) R. Tanaka, I. Suzuki, A. Yamaguchi, H. Misawa, H. Sakuragi, and K. Tokumaru, *Tetrahedron Lett.*, **33**, 3651 (1992).

2) R. A. Caldwell, S. N. Dhawan, and T. Majima, *J. Am. Chem. Soc.*, **106**, 6454 (1984).

3) J. C. Scaiano, *Tetrahedron*, **38**, 819 (1982).

4) J. C. Netto-Ferreira, V. Wintgens, and J. C. Scaiano, *J. Photochem. Photobiol. A: Chem.*, **57**, 153 (1991).

5) The cyclic ketones (2×10^{-3} mol dm^{-3}) were irradiated for 2–3 h under argon with a 400-W high-pressure mercury lamp through a K_2CrO_4-Na_2CO_3 filter solution. The products were isolated and their structures were determined on the basis of various spectral data. The yields of products were determined with GLPC.

6) The quantum yields were determined in comparison with the values for ring closure of a flugide, (*E*)-2-(2,5-dimethyl-3-furylethylidene)-3-isopropylidenebutanedioic acid anhydride (0.20 at 313 and 366 nm).7)

7) H. G. Heller and J. R. Langan, *J. Chem. Soc., Perkin 2*, **1981**, 341.

8) Laser flash photolyses were performed with 308-nm laser pulses from an excimer laser (Lambda Physik LPK-100) as an exciting light source and a pulsed xenon arc (Wacom KXL-151) as a monitoring light source. The details of the apparatus for laser flash photolysis have been described elsewhere.9)

9) H. Furuuchi, T. Arai, Y. Kuriyama, H. Sakuragi, and K. Tokumaru, *Chem. Phys. Lett.*, **162**, 211 (1989).

10) M. B. Zimmt, J. C. Doubleday, Jr., I. R. Gould, and N. J. Turro, *J. Am. Chem. Soc.*, **107**, 6724 (1985).

11) L. Salem and C. Rowland, *Angew. Chem., Int. Ed. Engl.*, **11**, 92 (1972).

12) The measurements were carried out in the temperature range of –6 – 40 °C for **1** and –8 – 41 °C for **2** to monitor the time profiles of transient absorptions at 337 nm.

13) M. B. Zimmt, J. C. Doubleday, Jr., and N. J. Turro, *J. Am. Chem. Soc.*, **108**, 3618 (1986).

14) The difference in E_a between **6** or **7** and **8** is due to the different intersystem crossing mechanisms.13)

15) L. Lunazzi, K. U. Ingold, and J. C. Scaiano, *J. Phys. Chem.*, **87**, 529 (1983).

16) K. C. Hwang, N. J. Turro, and J. C. Doubleday, Jr., *J. Am. Chem. Soc.*, **113**, 2850 (1991); N. Han, K. C. Hwang, X.-G. Lei, and N. J. Turro, *J. Photochem. Photobiol. A: Chem.*, **61**, 35 (1991).

17) Similar pulsed laser excitation of **2** in carbon tetrachloride exhibited an absorption due to a long-lived component with a lifetime longer than 50 μs in addition to those due to **7** and **8**.

18) R. A. Caldwell, H. Sakuragi, and T. Majima, *J. Am. Chem. Soc.*, **106**, 2471 (1984).

19) I. Suzuki, R. Nakagaki, H. Misawa, H. Sakuragi, K. Tokumaru, and S. Nagakura, unpublished results.

20) The absorption intensities were compared to that of benzophenone triplets in benzene as a reference.21) Molar extinction coefficients of the biradicals at the absorption maximum were reasonably assumed to be identical with that of diphenylmethyl radicals.22)

21) R. H. Compton, K. T. V. Grattan, and T. J. Morrow, *J. Photochem.*, **14**, 61 (1980).

22) J. Bartl, S. Steenken, H. Mayr, and R. A. McClelland, *J. Am. Chem. Soc.*, **112**, 6918 (1990).

23) P. J. Wagner, M. A. Meador, B. Zhou, and B.-S. Park, *J. Am. Chem. Soc.*, **113**, 9630 (1991).

(Received May 6, 1993)