Supplementary Material (ESI) for Organic & Biomolecular Chemistry

An ESR Analysis of the Mechanism of Pericyclic Reactions of Bicyclobutane

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Supporting Information

ESR experiments in the absence of a spin trapping agent

ESR measurements were carried out on a Bruker ElexSys E580 FT/CW X-band Spectrometer equipped with a Bruker ER 4118X-MD5 dielectric ring resonator. In addition, the temperature was adjusted with an Oxford 1TC 605 temperature controller. Each of **7a** and **7b** was dissolved in 0.05 mL of chloroform-*d* in a flask. A portion of the solution was introduced into an ESR tube with 2 mm inner diameter and then placed in the cavity. While the temperature was kept at 20^{o}C, ESR signals were recorded at X-band with the following conditions: modulation frequency 100 kHz; modulation amplitude 0.1 mT; time constant 20.48 ms; conversion time 40.96 ms; sweep time 83.88 s; receiver gain 60 dB; microwave power 1.995 mW.

We have also performed experiments with bicyclobutanes without any additives with exposure to light and found no signals in the ESR spectra.

ESR experiments in the presence of a spin trapping agent

Each of **7a**, **7b** and **7c** mixed with about 5–6 molar equivalents of MNP was dissolved in 0.05 mL of chloroform-*d* in a flask which was wrapped with aluminum foil in dark. Protected from light, a portion of the reaction mixture was introduced into an ESR tube with 2 mm inner diameter and then placed in the cavity. While the temperature was kept at 20^{o}C, ESR signals were recorded at X-band with the following conditions: modulation frequency 100 kHz; modulation amplitude 0.05 mT; time constant 20.48 ms; conversion time 40.96 ms; sweep time 167.77 s; receiver gain 60 dB; microwave power 1.995 mW.

As a control experiment, MNP (in the absence of bicyclobutane) was dissolved in 0.05 mL of chloroform-*d* in a flask which was wrapped with aluminum foil in dark. Protected from light, a portion of the solution was introduced into an ESR tube with 2 mm inner diameter and then placed in the cavity. Then, ESR signals were recorded (see Figure S5). This control experiment discussed below demonstrates that the data acquired from **7a** and **7b** was not due to degradation products of MNP by light or oxygen.

ESR spectra without a spin trapping agent

ESR spectra of radical species formed during the rearrangement of **7a** and **7b** are shown in Figure S1.

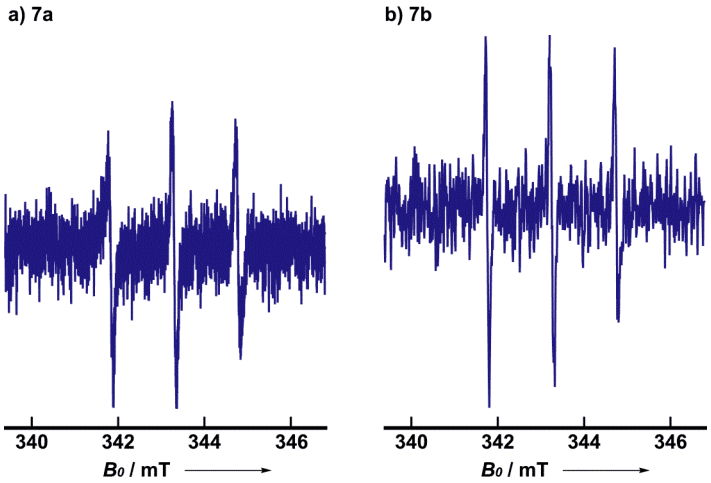

Figure S1. a) ESR spectrum of radical species generated from **7a** at a concentration of 1.5 M.
b) ESR spectrum of radical species generated from **7b** at a concentration of 1.5 M.

Noticeable signals disappear about 4 hours after the initiation of the reaction in both cases. It is difficult to interpret the spectra because of the low signal-to-noise ratio. The ESR signals can arise from either radical species involved in the reaction mechanism or oxidation products of the phosphamide moiety.

ESR intensity change with time

Figure S2 illustrates the change in integrated intensity of spin adducts generated from **7a** or **7b** and MNP. The intensity shown in a) or b) is the double-integral of the CW spectrum at a given time.

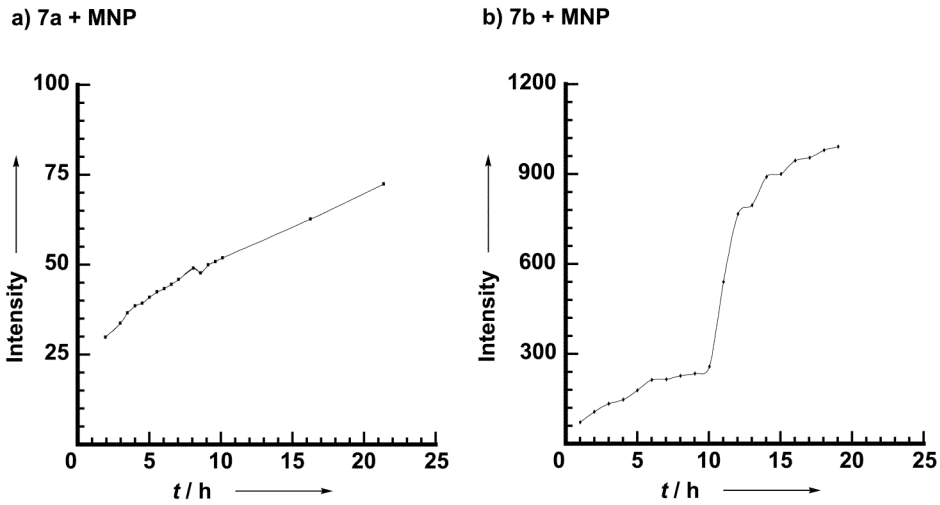

Figure S2. a) ESR signal intensity of spin adducts generated from **7a** and MNP (double-integration)
b) ESR signal intensity of spin adducts generated from **7b** and MNP (double-integration)

Signal intensity changes more rapidly for b) and the signal-to-noise ratio of b) is higher than a). The results are consistent with the fact that the rearrangement of **7b** is completed within 24 hours while >36 hours is needed for the rearrangement of **7a**.

Solvent-derived spin adducts

Figure S4 shows a comparison of spectra of MNP spin adducts generated from **7a** in both chloroform-*d* and benzene-d_6 and those generated from **7b** in chloroform-*d*.

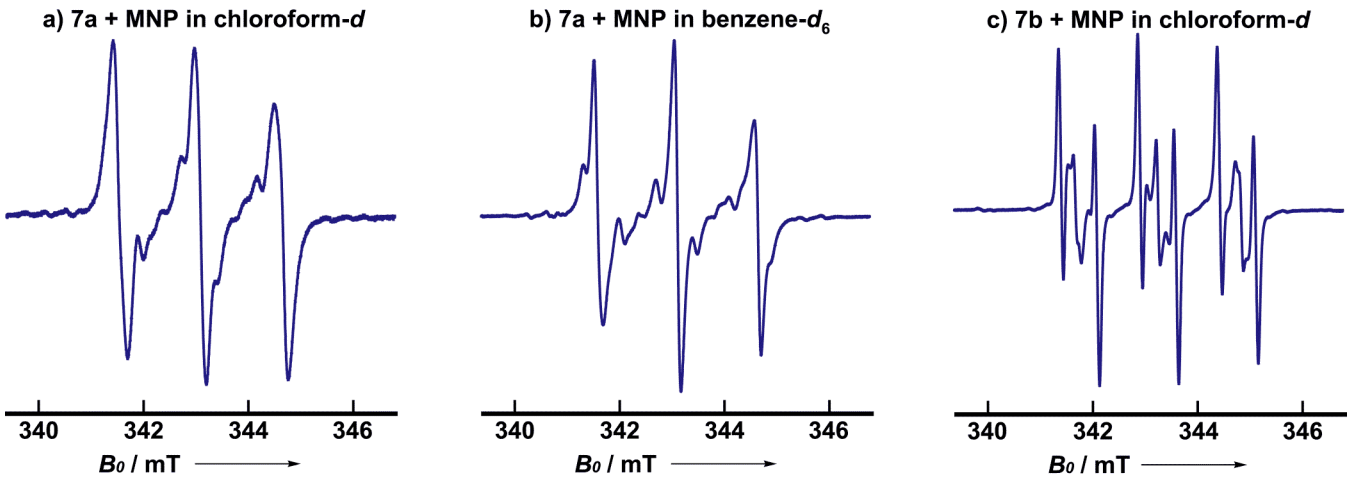

Figure S4. a) ESR spectrum of MNP spin adducts formed from **7a** in chloroform-*d*
b) ESR spectrum of MNP spin adducts formed from **7a** in benzene-d_6
c) ESR spectrum of MNP spin adducts formed from **7b** in chloroform-*d*

- Hyperfine coupling constants of spectrum a) **7a** + MNP in chloroform-*d*
a^N (primary) = 1.43 mT
a^H (CH_2) = 0.31 mT
a^H (CH) = 0.01 mT
a^N (tertiary) = 1.56 mT
ΔH = 0.23 mT

- Hyperfine coupling constants of spectrum b) **7a** + MNP in benzene-d_6
a^N (primary) = 1.43 mT
a^H (CH_2) = 0.31 mT
a^H (CH) = 0.01 mT
a^N (tertiary) = 1.55 mT
ΔH = 0.15 mT

The change of solvent from chloroform-*d* to benzene-d_6 only leads to a slight change in hyperfine coupling constants as shown in Figure S4. Since these solvents have different structures, the similarity in hyperfine coupling constants rules out the possibility of the solvent-derived spin adducts as major contributors to the spectrum. In addition, the spectrum of **7b** and MNP in chloroform-*d* is different from the spectrum of **7a** and MNP in the same solvent, which indicates that solvent-derived spin adducts would not be major components even if they existed.

ESR experiment and simulation of 7b

Figure S3 shows a comparison of the experimental data of **7b** with simulated spectra based on the proposed radical structures.

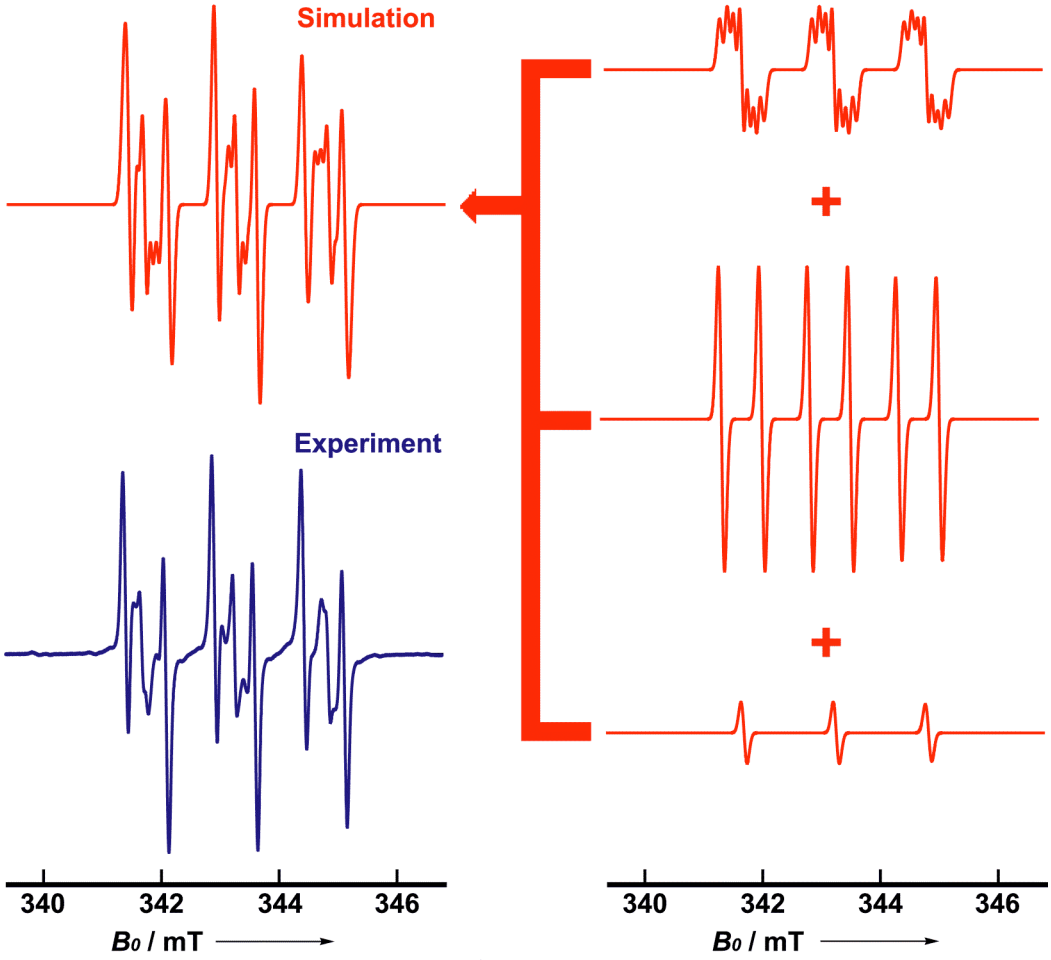

Figure S3. Experimental and simulated ESR spectra of MNP spin adducts formed from **7b**.

The simulated spectrum corresponding to three radical moieties shows a good agreement with the experimental data.

ESR signals from MNP

Figure S5 shows a comparison of spectra of radical species generated from MNP in chloroform-*d* obtained before and after exposure to light.

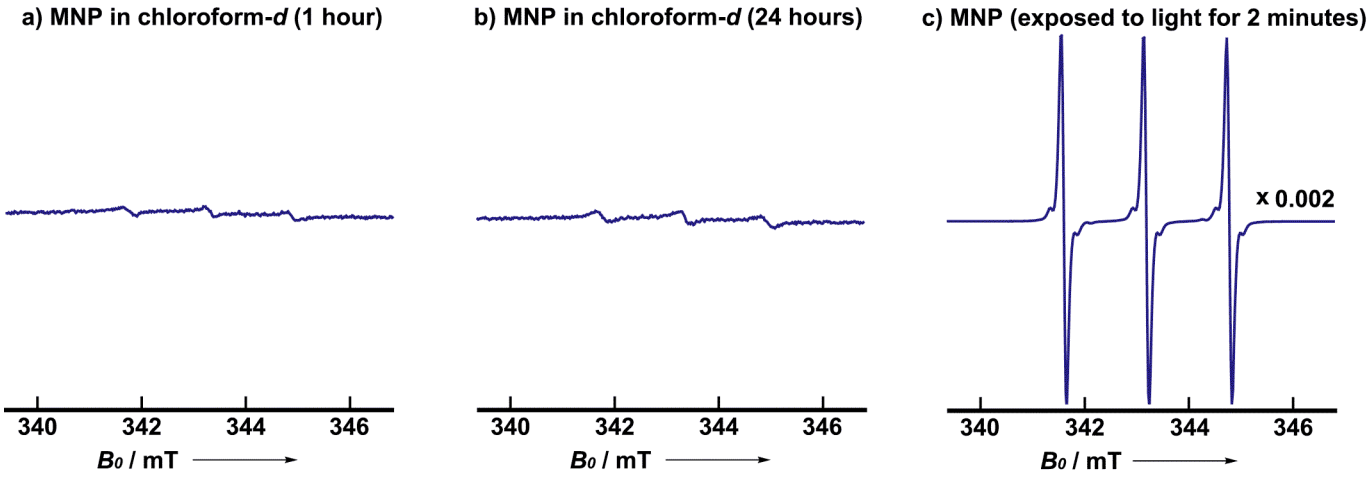

Figure S5. a) ESR spectrum of 4.5 M MNP in chloroform-*d* (1 hour)
b) ESR spectrum of 4.5 M MNP in chloroform-*d* (24 hours)
c) ESR spectrum of 4.5 M MNP in chloroform-*d* (after exposure to light for 2 minutes)

No significant change in signal intensity was observed even after ~24 h. After the ESR tube had been exposed to light for about 2 min, however, three very large lines emerged in the ESR spectrum. The result indicates that MNP, which otherwise would have been converted to an ESR active compound by light, was well protected from light. Thus, we assume that there was very little chance for the light-protected samples to be affected by oxygen or exposure to UV.

NMR kinetics experiments

^{1}H NMR kinetic studies were carried out on 500 MHz or 600 MHz Bruker-Avance instruments. Freshly prepared **7a** and **7b** were dissolved in $CDCl_3$ (0.1 M initial concentrations) and NMR spectra were recorded at 0.5 h and 0.25 h time intervals for **7a** and **7b**, respectively. The rate constants are calculated based on the disappearance of the starting materials.

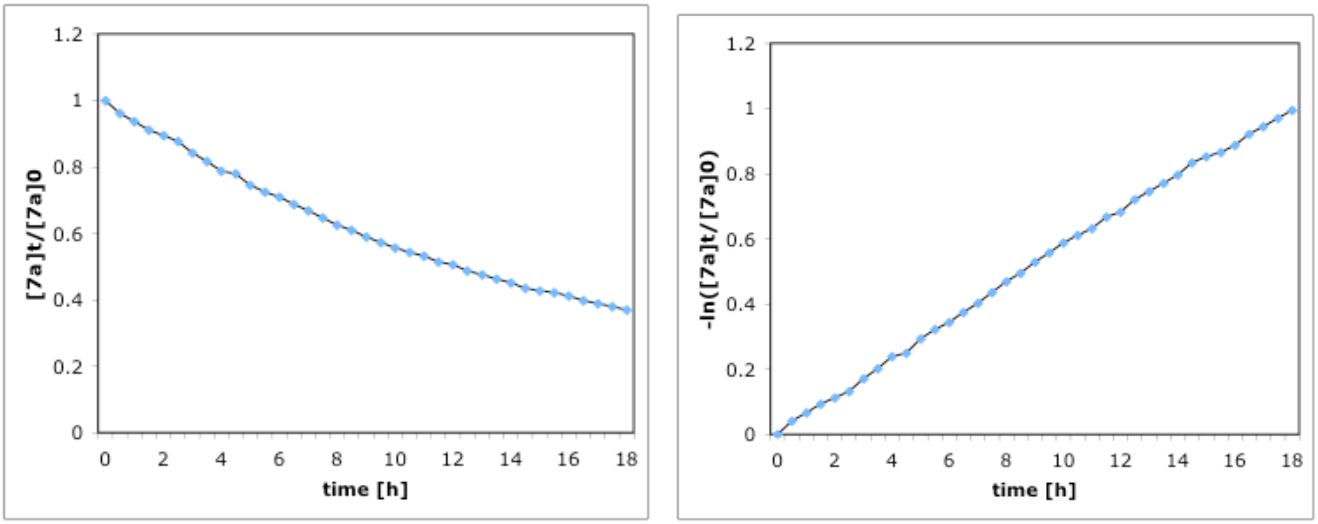

Chart 1. The graph of concentration vs. time for the rearrangement of **7a**.

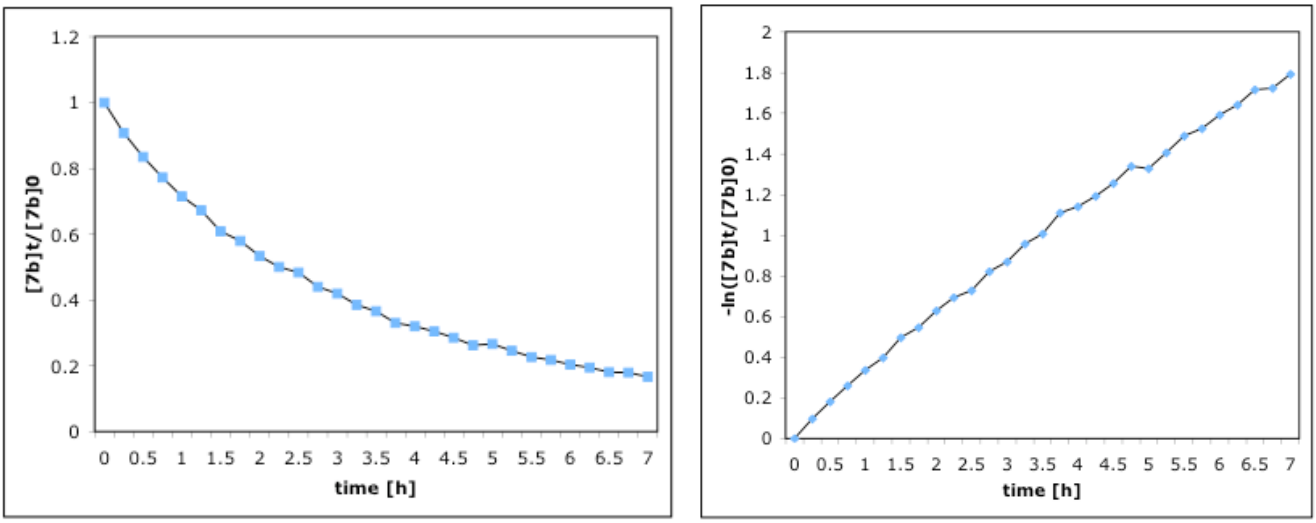

Chart 2. The graph of concentration vs. time for the rearrangement of **7b**.