Supporting Information for

Reaction Cavities of Liquid and Solid Phases of a Long *n*-Alkane, *n*-Nonadecane, as Probed by the Regio- and Stereo-Chemical Fates of Two Singlet Radical Pairs

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Results from Irradiations of (R)-2 in n-Nonadecane

Both the **2BN**/**4BN** product ratios and *ee*s of the remaining **2** vary with its degree of conversion upon irradiation in *n*-nonadecane. The presence of a significant amount of (*S*)-**2** at higher conversions of (*R*)-**2** requires that both enantiomers be considered in analyses of the reactions, including those dealing with the kinetics. Furthermore, secondary photoreactions of **2BN** and **4BN**[1] or of their keto precursors prior to tautomerization[2] can also complicate analyses. However, at conversions approaching 0%, the amount of (*S*)-**2** and secondary photoproducts are mechanistically inconsequential. Therefore, the relative yields in hexane and the other media reported in Table 2 have been extrapolated to 0% conversion of (*R*)-**2** using linear regressions of data from conversions in the range of 2-30%.

Table S1. Product distributions[a] from reactions of (*R*)-**2** in the hexagonal phase of *n*-nonadecane at 25 °C.

% Conversion of (*R*)-**2**	**2BN**	**4BN**	**3**	**5**	**2BN/4BN**
3	21.6±1.3	40.8±1.9	19.3±1.3	18.4±1.0	0.53±0.04
5	19.6±1.1	40.7±2.5	21.7±1.1	17.9±1.0	0.48±0.04
7	18.9±1.1	40.9±1.7	24.9±1.6	15.3±1.0	0.46±0.03
8	17.4±1.1	40.6±1.8	25.3±1.5	16.7±1.0	0.43±0.03
10	17.5±0.5	39.7±0.5	26.8±1.0	16.1±1.0	0.44±0.03
11	14.8±0.5	40.5±0.5	30.5±1.0	14.3±1.0	0.37±0.02
14	13.8±0.5	40.0±2.2	30.1±1.1	16.1±1.0	0.35±0.02
15	13.9±0.5	41.3±0.5	32.3±1.3	12.5±1.0	0.34±0.02

[a] Relative yield (%); the sum of all products is taken as 100%; mass balance is > 80%.

Table S2. *Ee*% of products from irradiations of (*R)*-**2** in the hexagonal phase of *n*-nonadecane at 25 °C.[a]

% Conversion of (*R*)-**2**	*ee%* remaining **2**[b]	 **2BN**	 **4BN**
3	99.2	56.6	29.0
5	99.0	56.4	28.8
7	98.6	54.0	28.6
8	98.4	51.1	27.7
10	98.0	53.2	27.8
11	98.0	51.6	28.0
14	97.6	50.8	26.8
15	97.2	49.6	26.6

[a] ± 1.0%; *ee* of (*R*)-**2** before irradiation is 99.5%. [b] (*R*)-enantiomer in excess.

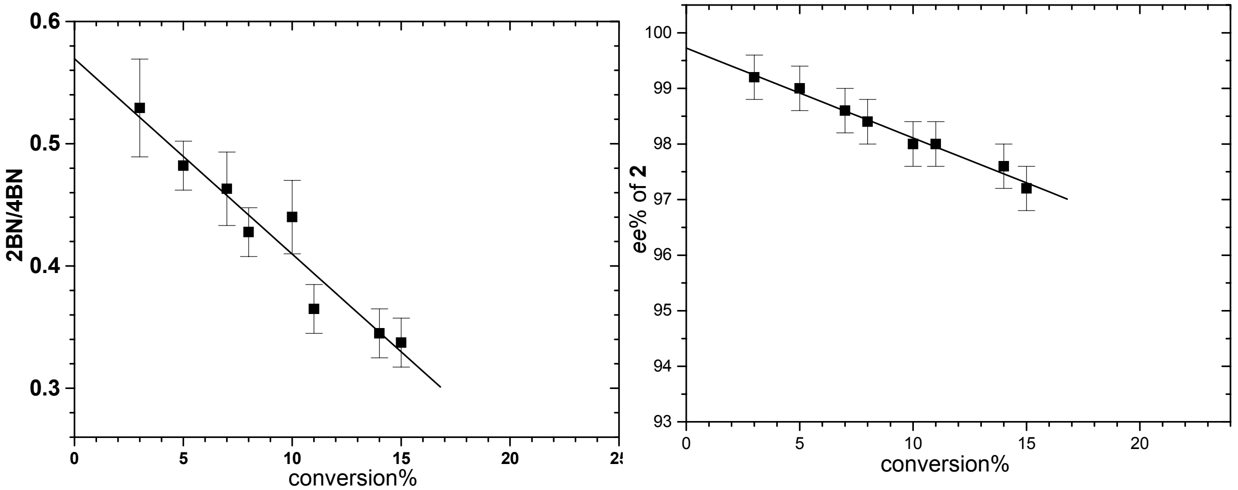

Figure S1. The **2BN**/**4BN** product ratio (left) and *ee%* of **2** (right) *versus* % conversion for irradiations of (*R*)-**2** in *n*-nonadecane at 25 °C.

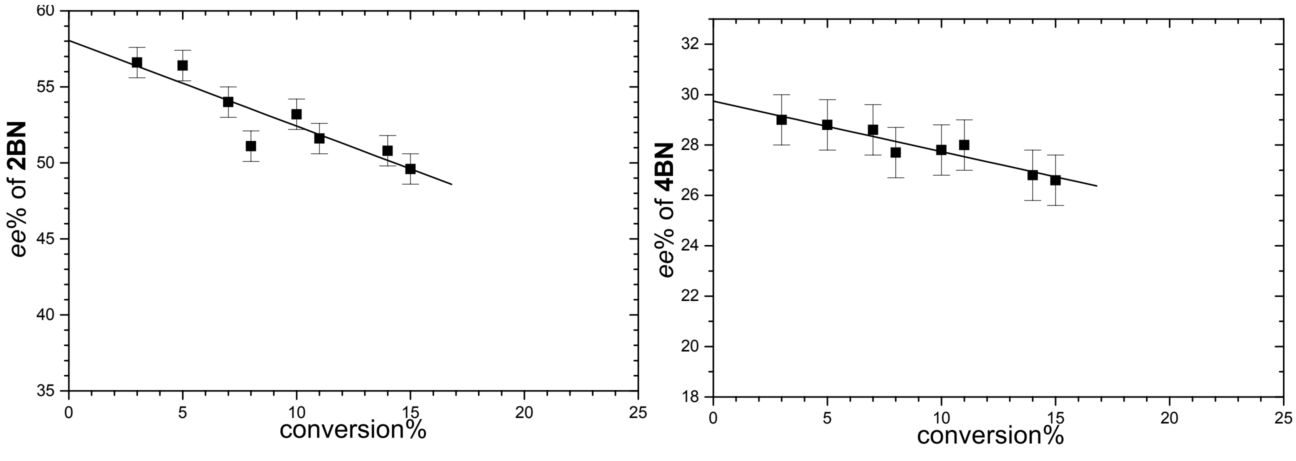

Figure S2. *Ee%* of **2BN** (left) and **4BN** (right) *versus* % conversion for irradiations of (*R*)-**2** in *n*-nonadecane at 25 °C.

Table S3. Product distributions[a] from reactions of (*R*)-**2** in the orthorhombic phase of *n*-nonadecane at 5 °C.

% Conversion of (*R*)-**2**	**2BN**	**4BN**	**3**	**5**	**2BN/4BN**
1	23.5±1.8	42.5±1.8	25.4±1.8	8.6±1.0	0.55±0.04
2	22.3±1.0	44.8±1.0	24.8±1.0	8.1±1.0	0.50±0.04
4	17.6±1.0	43.4±1.0	31.7±1.0	7.3±1.0	0.41±0.04
5	18.6±0.8	45.0±1.7	26.9±1.4	9.5±1.0	0.41±0.04
7	7.7±1.5	35.6±1.5	49.9±1.5	6.8±1.0	0.22±0.04

[a] Relative yield (%); the sum of all products is taken as 100%; mass balance is > 80%.

Table S4. *Ee*% of products from reactions of (*R)*-**2** in the orthorhombic phase of *n*-nonadecane at 5 °C.[a]

% Conversion of (*R*)-**2**	*ee%*		
	remaining **2**[b]	**2BN**	**4BN**
1	99.2	61.4	31.9
2	99.0	58.9	32.3
4	98.8	58.0	31.9
7	98.0	55.4	32.0
7	98.4	55.8	31.2
14	97.8	54.6	31.8

[a] ± 1.0%; *ee* of (*R*)-**2** before irradiation is 99.5%. [b] (*R*)-enantiomer in excess

References

[1] Both **2BN** and **4BN** have strong absorbances at ca. 280-320nm (i.e., within the wavelength region of irradiation). Control experiments demonstrate that: (1) photolysis of **2BN** produces a small amount (ca. 10%) of **4BN** and other compounds, but **4BN** does not generate **2BN**; (2) the disappearance rate of **2BN** is much faster than that of **4BN** when their mixture is irradiated at > 300 nm.

[2] (a) M. C. Jiménez, M. A. Miranda, J. C. Scaiano and R. Tormos, Two-photon processes in the photo-Claisen and photo-Fries rearrangements. Direct observation of dienic ketenes generated by photolysis of transient cyclohexa-2,4-dienones, *Chem. Commun.*, 1997, **16**, 1487-1488; (b) T. Mori, M. Takamoto, H. Saito, T. Furo, T. Wada and Y. Inoue, Remarkable differences in photo and thermal (acid-catalyzed) reactivities between *ortho*- and *para*-acylcyclohexadienones as essential factors determining the overall efficiency of the photo-Fries rearrangement, *Chem. Lett.*, 2004, **33**, 256-257.