Supplementary Material (ESI) for Photochemical & Photobiological Sciences

Supplementary Information Product Studies

Photolysis of 2 in 1:1 CH_3CN:H_2O at pH 1, 7, and 12. A 50 mg (2.7×10^{-4} mol) sample of **2** was dissolved in CH_3CN (50 mL), a 50 mL aliquot of H_2O was added (whose pH had been adjusted by the addition of either 1 M HCl or NaOH as needed), and the resulting solution irradiated for 30 min. Following workup and extraction as described above, evaporation of the residual organic solvent gave the crude photoproduct mixture. The major product, **3** (34 mg, 1.8×10^{-4} mol; 35 mg, 1.9×10^{-4} mol; and 31 mg, 1.7×10^{-4} mol), was separated by prep-TLC (CH_2Cl_2) in 70%, 74%, and 65% yields for pH 1, 7, and 12, respectively, at >95% conversion of starting material.

Photolysis of 2 in Benzene. A 50 mg (2.7×10^{-4} mol) sample of **2** was dissolved in benzene (100 mL) and irradiated for 60 min. Evaporation of the solvent gave the crude photoproduct mixture. ^{1}H NMR and MS (EI) suggested ca. 20% conversion to **3** (33% yield), ca. 40% unreacted starting material, and 15% yield (3.7 mg; 2.4×10^{-5} mol) of biphenyl (m/z=153 [M^+-1]) which was separated by prep-TLC (1:1 CH_2Cl_2:hexane) and whose ^{1}H NMR was compared to a sample of commercially available authentic compound.

Photolysis of 2 in Cyclohexane. A 50 mg (2.7×10^{-4} mol) sample of **2** was dissolved in spectral grade cyclohexane (100 mL) and irradiated for 60 min. Evaporation of the solvent gave the crude photoproduct mixture. ^{1}H NMR and MS (EI) suggested ca. 34% conversion to **3** (68% yield) and ca. 50% unreacted starting material.

Photolysis of 2 in Diethyl Ether. A 50 mg (2.7×10^{-4} mol) sample of **2** was dissolved in diethyl ether (100 mL) and irradiated for 60 min. Evaporation of the solvent gave the crude photoproduct mixture. ^{1}H NMR and MS (EI) suggested ca. 31% conversion to **2** (62% yield) and ca. 50% unreacted starting material.

Photolysis of 2 in Ethyl Acetate. A 50 mg (2.7×10^{-4} mol) sample of **2** was dissolved in ethyl acetate (100 mL) and irradiated for 60 min. Evaporation of the solvent gave the crude photoproduct mixture. ^{1}H NMR and MS (EI) suggested ca. 25% conversion to **3** (50% yield) and ca. 50% unreacted starting material.

Photolysis of 2 in Hexane. A 50 mg (2.7×10^{-4} mol) sample of **2** was dissolved in spectral grade hexane (100 mL) and irradiated for 60 min. Evaporation of the solvent gave the crude photoproduct mixture. ^{1}H NMR and MS (EI) suggested ca. 41% conversion to **3** (81% yield) and ca. 50% unreacted starting material.

Photolysis of 2 in Toluene. A 50 mg (2.7×10^{-4} mol) sample of **2** was dissolved in toluene (100 mL) and irradiated for 60 min. Evaporation of the solvent gave the crude photoproduct mixture. ^{1}H NMR and MS (EI) suggested ca. 23% conversion to **3** (58% yield), ca. 60% unreacted starting material, and 12% yield (5.9 mg; 3.2×10^{-5} mol) of bibenzyl (m/z=182 [M^+], 91 [M^+-C_7H_7]) which was separated by preparative TLC (1:1 CH_2Cl_2:hexane) and whose ^{1}H NMR was compared to a sample of commercially available authentic compound.

Photolysis of 2 in 1-Butanol. A 50 mg (2.7×10^{-4} mol) sample of **2** was dissolved in 1-butanol (100 mL) and irradiated for 30 min. Evaporation of the solvent gave the crude photoproduct mixture. ^{1}H NMR and MS (EI) suggested ca. 82% conversion to **3** (91% yield) and ca. 10% unreacted starting material.

Photolysis of 2 in *t*-Butanol. A 50 mg (2.7×10^{-4} mol) sample of **2** was dissolved in *t*-butanol (100 mL) and irradiated for 30 min. Evaporation of the solvent gave the crude photoproduct mixture. ^{1}H NMR and MS (EI) suggested ca. 65% conversion to **3** (93% yield) and ca. 30% unreacted starting material.

Photolysis of 2 in Ethanol. A 50 mg (2.7×10^{-4} mol) sample of **2** was dissolved in anhydrous ethanol (100 mL) and irradiated for 30 min. Evaporation of the solvent gave the crude photoproduct mixture. ^{1}H NMR and MS (EI) suggested ca. 70% conversion to **3** (93% yield) and ca. 25% unreacted starting material.

Photolysis of 2 in Methanol. A 50 mg (2.7×10^{-4} mol) sample of **2** was dissolved in methanol (100 mL) and irradiated for 30 min. Evaporation of the solvent gave the crude photoproduct mixture. ^{1}H NMR and MS (EI) suggested ca. 67% conversion to **3** (96% yield) and ca. 30% unreacted starting material.

Photolysis of 2 in 2-Propanol. A 50 mg (2.7×10^{-4} mol) sample of **3** was dissolved in 2-propanol (100 mL) and irradiated for 30 min. Evaporation of the solvent gave the crude photoproduct mixture. ^{1}H NMR and MS (EI) suggested ca. 60% conversion to **3** (92% yield) and ca. 35% unreacted starting material.

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Supplementary Information Tables

Table S1 Rate constants (in s^{-1}) and deuterium isotope effects for the first-order thermal decays of 2,2'-biphenylquinones **9**, **20**, **21**, and **22** in acetonitrile (k_H) and acetonitrile-d_3 (k_D). Error bars are the range of duplicate trials.

Compound	k_H	k_D	k_H/k_D
9	$8.87\pm0.21\times10^{-3}$	$7.08\pm0.11\times10^{-3}$	1.25±0.05
20	$2.25\pm0.07\times10^{-2}$	$2.30\pm0.02\times10^{-2}$	0.98±0.04
21	$2.86\pm0.01\times10^{-2}$	$2.91\pm0.05\times10^{-2}$	0.98±0.02
22	$7.09\pm0.14\times10^{-3}$	$6.13\pm0.37\times10^{-3}$	1.16±0.07

Table S2 Rate constants (in s^{-1}) and deuterium isotope effects for the first-order thermal decays of 2,2'-biphenylquinones **9**, **20**, **21**, and **22** in benzene (k_H) and benzene-d_6 (k_D). Error bars are the range of duplicate trials.

Compound	k_H	k_D	k_H/k_D
9	$2.93\pm0.10\times10^{-2}$	$2.32\pm0.14\times10^{-2}$	1.26±0.10
20	$6.93\pm0.40\times10^{-3}$	$6.60\pm0.62\times10^{-3}$	1.05±0.15
21	$2.40\pm0.07\times10^{-2}$	$2.37\pm0.09\times10^{-2}$	1.01±0.07
22	$2.34\pm0.04\times10^{-2}$	$2.19\pm0.02\times10^{-2}$	1.07±0.03

Table S3 Rate constants (in s^{-1}) and deuterium isotope effects for the first-order thermal decays of 2,2'-biphenylquinones **9**, **20**, **21**, and **22** in toluene (k_H) and toluene-d_8 (k_D). Error bars are the range of duplicate trials.

Compound	k_H	k_D	k_H/k_D
9	$2.83\pm0.14\times10^{-2}$	$2.38\pm0.12\times10^{-2}$	1.19±0.12
20	$6.99\pm0.05\times10^{-3}$	$6.74\pm0.09\times10^{-3}$	1.04±0.03
21	$2.07\pm0.03\times10^{-2}$	$2.05\pm0.08\times10^{-2}$	1.01±0.05
22	$2.10\pm0.12\times10^{-2}$	$1.81\pm0.05\times10^{-2}$	1.16±0.10

Table S4 Field (F) and resonance (R) substituent constants and absolute and relative rate constants for the rearrangement of **11**, **35**, **36**, **37**, **38**, and **39** into the corresponding 2,2'-biphenylquinones used in the Swain-Lupton modeling approach.

Compound	ΣF	ΣR	k (s^{-1})	$\ln(k/k_o)$
11	0	0	4.9×10^{3}	0
35	-0.04	-0.82	7.2×10^{4}	2.7
36	0.72	-0.24	6.8×10^{3}	0.33
37	1.08	-3.36	9.9×10^{7}	9.9
38	0.72	-0.24	6.8×10^{3}	0.22
39	5.76	-0.96	5.5×10^{4}	0.11

Supplementary Information Figures

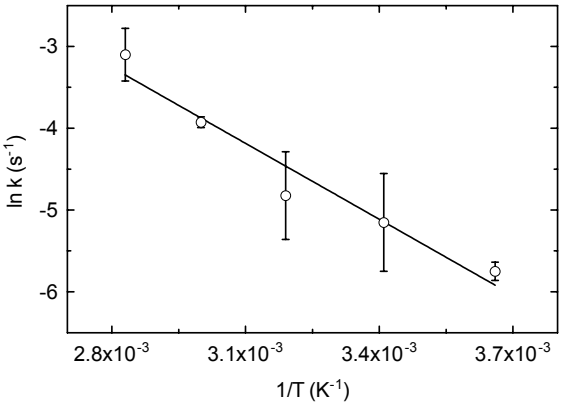

Fig. S1 Arrhenius plot for the thermal decay of 2,2'biphenylquinone (**9**) in dry CH_3CN. Error bars are 95% confidence limits on the mean.

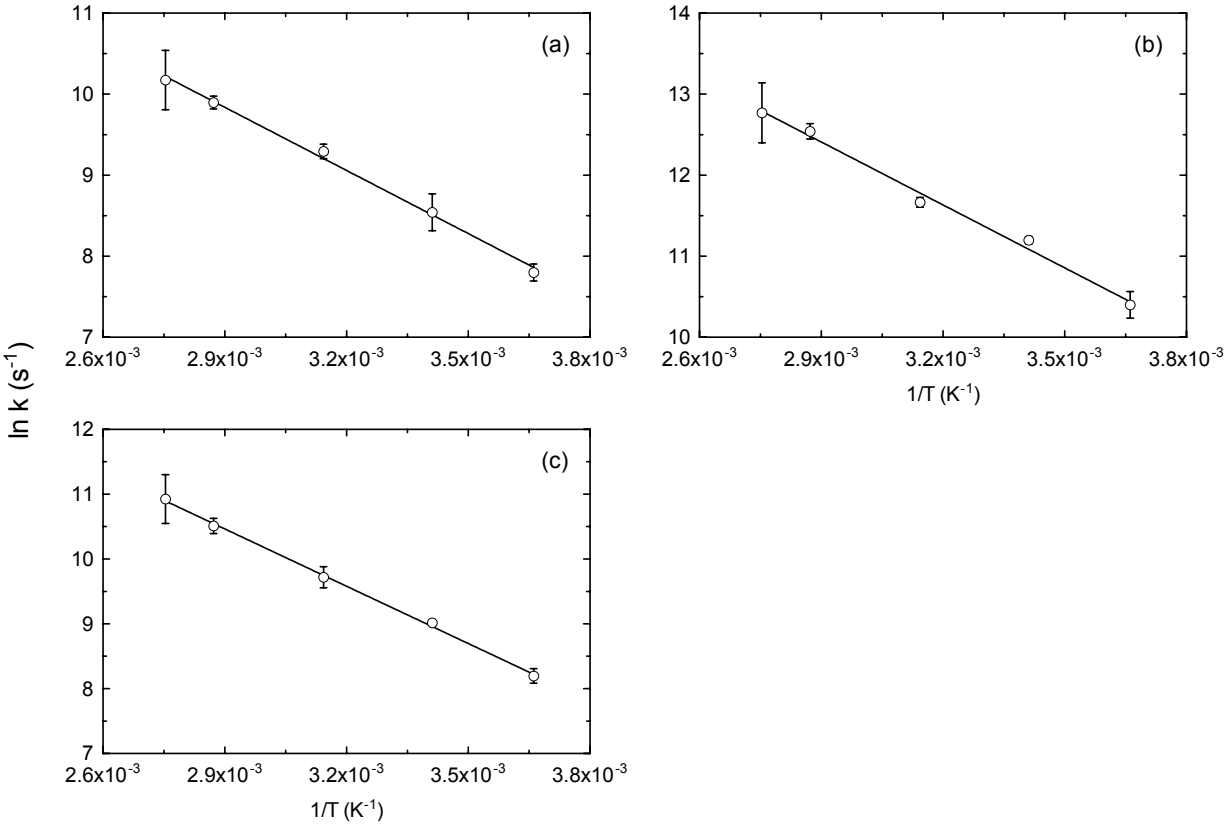

Fig. S2 Arrhenius plots for the rearrangement of 2-spiro-6'-cyclohexa-2',4'-dien-1'-ones (a) **11**, (b) **35**, and (c) **36** into the corresponding 2,2'-biphenylquinones. Error bars are 95% confidence limits on the mean.