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Full Paper

Formation and Direct Detection of Non-Conjugated Triplet 1,2-Biradical from β , γ -Vinylarylketone

H. Dushanee M. Sriyarathne,^A Kosala R. S. Thenna-Hewa,^A Tianeka Scott,^A and Anna D. Gudmundsdottir^{A,B}

^ADepartment of Chemistry, University of Cincinnati, Cincinnati, OH 45221, USA. ^BCorresponding author. Email: anna.gudmundsdottir@uc.edu

Laser flash photolysis of 2-methyl-1-phenylbut-3-en-1-one (1) conducted at irradiation wavelengths of 266 and 308 nm results in the formation of triplet 1,2-biradical **2** that has λ_{max} at 370 and 480 nm. Biradical **2** is formed with a rate constant of $1.1 \times 10^7 \text{ s}^{-1}$ and decays with a rate constant of $2.3 \times 10^5 \text{ s}^{-1}$. Isoprene-quenching studies support the notion that biradical **2** is formed by energy transfer from the triplet-excited state of the ketone chromophore of **1**. Density functional theory calculations were used to verify the characterization of triplet biradical **2** and validate the mechanism for its formation. Thus, it has been demonstrated that intramolecular sensitization of simple alkenes can be used to form triplet 1,2-biradicals with the two radical centres localized on the adjacent carbon atoms.

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Introduction

Nature elegantly converts light into molecular actions in various biological systems. For example, light-activated *trans-cis* isomerization in the retinal rods of the eye is an important process in the vision of most vertebrates.^[1] Similarly, light-initiated isomerization of simple alkenes has been used in various applications such as the activation of photoremovable protecting group.^[2–5] Detailed knowledge of the isomerization mechanisms is essential to develop photoswitches and photoremovable protecting groups that can be tailored to specific applications. Direct irradiation of simple alkenes results in fast *cis-trans* isomerization on their singlet-excited surface, and the isomerization is generally not affected by molecular oxygen.^[6–8] *Cis-trans* isomerization can, however, also take place on the triplet-excited

surface of alkenes through the formation of 1,2-biradicals. As the intersystem crossing from the singlet-excited states of simple alkenes to their triplet-excited states is generally not efficient, 1,2-biradicals have only been studied sporadically as their formation typically requires triplet sensitization.^[9,10] The limited knowledge of *trans-cis* isomerization through 1,2-biradicals restricts their potential use in applications.

Recently, we reported that the α,β -vinylarylketones undergo *cis–trans* isomerization upon irradiation. Excitation at shorter wavelengths results in efficient isomerization on the singlet surface.^[11] In comparison, irradiation at longer wavelengths consequently yields *cis–trans* isomerization on the triplet surface through the formation of 1,2-biradicals (Scheme 1). Irradiation at wavelengths above 300 nm selectively forms the triplet-excited state of the arylketone chromophore, which





rearranges to form the subsequent 1,2-biradicals. The lifetimes of these biradicals are of a few microseconds and they decay by intersystem crossing to form the *trans* and *cis* isomers of their precursors. Density functional theory (DFT) calculations show that the radical centred on the α -carbon atom is stabilized by conjugation with the ketone chromophore, whereas the radical on the β -carbon atom is entirely localized on that carbon atom.

Caldwell et al. showed that 1,2-biradicals formed from irradiating styrene derivatives results in 1,2-biradicals, and their lifetimes are affected by their flexibility. Flexible acyclic 1,2-biradicals have lifetimes on the order of a few nanoseconds, whereas the rigid cyclic derivatives have significantly longer lifetimes (Chart 1).^[12] Comparably, García-Expósito et al. revealed that irradiation of 2-pentenoate ester derivatives results in triplet 1,2-biradicals that have lifetimes of a few microseconds.^[13] The styrene biradicals are stabilized by conjugation with the phenyl group, and, similarly, the pentenoate ester biradicals are stabilized by conjugation with the adjacent carbonyl moiety. Nguyen et al. preformed ab initio calculation to optimize the relaxed twisted triplet excited state of ethylene or the triplet 1,2-ethylene biradical; it was between 62 and 66 kcal mol^{-1} above its ground state. Furthermore, the triplet 1,2-ethylene biradical has been experimentally estimated to be 58 ± 3 kcal mol⁻¹ above its ground state.^[14,15]

In this paper, we report the photochemistry of β , γ -vinylarylketone with a built-in triplet sensitizer. Flash photolysis of vinylketone **1** (Chart 2) using irradiation wavelengths of 266 and 308 nm results in the formation of its triplet-excited state that undergoes energy transfer to form 1,2-biradical **2**, which has the radical centres localized on the β and γ atoms. The triplet biradical has λ_{max} at 370 and 480 nm, a lifetime of 4.3 µs, and decays by intersystem crossing to reform **1**.

Results

Laser Flash Photolysis

Laser flash photolysis^[16-17] studies of 1 were performed to identify the excited states and intermediates formed upon excitation of 1. The argon-saturated acetonitrile laser flash photolysis of 1 produced a transient absorption with λ_{max} at \sim 370 and \sim 480 nm (Fig. 1). These absorption bands were assigned to have contributions from both the first triplet-excited state (T_{1K}) of 1 and triplet biradical 2 based on their timedependent density functional theory (TD-DFT)-calculated spectra (see Calculations below for details). The calculations place the major electron transition for T_{1K} of 1 in acetonitrile at 301 (f=0.0598), 306 (f=0.0226), 357 (f=0.0132), 402 (f = 0.0659), and 407 (f = 0.0142) and for biradical 2 in acetonitrile at 362 (f = 0.0160) and 466 (f = 0.0332) nm (f denotes calculated oscillator strength). The results fit well with the experimentally observed spectra (Fig. 1). A similar transient absorption was obtained in methanol, hexane, toluene, and dichloromethane.

To further support the spectral assignment, the kinetic analysis of the transient absorption was performed at 360 and 480 nm; the kinetic profiles at 360 and 480 nm were the same, and thus the absorptions at these two wavelengths belong to the same intermediates. At shorter time scales, the transient absorption was formed with a rate constant of $1.12 \times 10^7 \text{ s}^{-1}$ ($\tau = \text{lifetime} = 89 \text{ ns}$, Fig. 2). At longer time scales, it decays with a rate constant of $2.33 \times 10^5 \text{ s}^{-1}$. We assign the faster rate constant to the rate of formation of biradical **2** from T_{1K} of **1**, and thus T_{1K} of **1** has a lifetime of 89 ns. The slower rate constant is



Chart 1. 1,2-Biradicals formed from styrene and pentenoate ester derivatives.







Fig. 1. (a) Laser flash photolysis of 1 in argon-saturated acetonitrile. TD-DFT-calculated spectra of (b) biradical 2 and (c) T_{1K} of 1 in acetonitrile.

the decay rate constant of biradical **2** that has a lifetime of $\sim 4.3 \,\mu s$. Furthermore, the laser flash photolysis of **1** in oxygensaturated acetonitrile demonstrated that oxygen quenched all the transient absorption, presumably as oxygen efficiently quenched T_{1K} of **1** and biradical **2**.

Additional support for the assignments of the transient absorption came from the isoprene-quenching studies (Fig. 3). Increasing isoprene concentrations reduced the yields of the transient absorption at 480 nm, but the rate of decay of the transient absorption was not affected, thus conforming that the absorption is due to biradical **2**, which is not quenched by isoprene, but its precursor, T_{1K} of **1**. We used the Stern–Volmer Eqn 1 to obtain the Stern–Vomer plot displayed in Fig. 3.^[18]

$$\frac{A_0}{A} = 1 + k_q \tau_0[Q] \tag{1}$$

In the Stern–Volmer equation A_0 is the absorption of biradical **2** without any quencher, A is the absorption of biradical **2** at



Fig. 2. Kinetic traces at 480 nm at (a) longer and (b) shorter timescales.



Fig. 3. Stern–Volmer plot obtained upon quenching the absorption at 480 nm with isoprene.

various isoprene concentrations, k_q is the quenching rate constant of the triplet state, τ_0 is the lifetime of T_{1K} of 1 without any isoprene, and [*Q*] is the concentration of the isoprene.

The Stern–Volmer plot of A_0/A versus isoprene concentration can be fitted as a straight line with a slope of $1.2 \times 10^4 \,\mathrm{M^{-1}}$. By assuming diffusion-controlled quenching or k_q is between 1 and $10 \times 10^9 \,\mathrm{M^{-1}s^{-1}}$, it can estimated that the lifetime of T_{1K} of 1 is between 1200 and 120 ns, which fits reasonably with the lifetime obtained directly from the rate of formation of biradical 2. We did not attempt to measure the effect of isoprene on the rate of formation of biradical 2 as it is comparable to the time resolution of the laser (~17 ns),^[16] and thus, it is difficult to obtain accurate data.

The laser flash photolysis of 1 in argon-saturated acetonitrile was also performed at irradiation wavelength of 266 nm, resulting in a transient spectrum with λ_{max} at 360 and 480 nm (Fig. 4). This transient spectrum is similar to the one obtained using irradiation wavelength of 308 nm. In addition, no negative absorption was observed around 350 nm, and thus it was possible to obtain a transient absorption at shorter wavelengths. Because irradiation with a 266-nm laser requires a lower concentration of 1, the extent of bleaching of the starting material around 350 nm is smaller.

Kinetic analysis of the absorption at 360 and 480 nm reveals that both wavelengths have the same kinetic profile. The rate of forming the transient absorption is $1.38 \times 10^7 \text{ s}^{-1}$ ($\tau \sim 75 \text{ ns}$), and it decays with a rate constant of $2.34 \times 10^5 \text{ s}^{-1}$ ($\tau \sim 4.3 \text{ µs}$).

We demonstrated that the transient absorption obtained by laser flash photolysis of acetophenone is quenched with crotyl chloride (see Supplementary Material). The triplet-excited state of acetophenone is quenched by energy transfer to crotyl chloride with a rate constant of $1.2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$, thus, further supporting that the energy transfer from triplet ketones to simple alkenes is feasible.



Fig. 4. Laser flash photolysis of **1** with 266 nm irradiation in argonsaturated acetonitrile: (a) transient absorption spectrum and kinetic traces at 480 nm at (b) longer and (c) shorter timescales.

The laser flash photolysis of **1** demonstrates that upon irradiation, **1** forms a T_{1K} that decays by energy transfer to form triplet biradical **2**. The photochemistry of **1** is not affected by the irradiation wavelength, thus indicating that the ketone chromophore in **1** absorbs more significantly than the vinyl moiety at 308 and 266 nm. Based on the laser flash photolysis, we propose that the mechanism for forming biradical **2** is as displayed in Scheme 2.

Calculations

The stationary points on the singlet and triplet surface of **1** were calculated using *Gaussian09* at the B3LYP level of theory and with the 6-31+G(d) basis set^[19-21] to better understand the factors governing its photochemistry and the formation of triplet biradical **2**. In addition, we calculated the TD-DFT spectra for the optimized structures of T_{1K} of **1** and biradical **2** to aid with their characterization using laser flash photolysis (Fig. 1b, c).

We used the TD-DFT calculations to locate the first singletexcited state (S1) and the first and second triplet-excited states $(T_{1K} \text{ and } T_{2K}) \text{ of } 1$. The calculations revealed that $S_{1K} \text{ of } 1$ was at 83 kcal mol⁻¹ above its ground state (S₀), T_{1K} of 1 was at 72 kcal mol^{-1} above its S₀, and T_{2K} was only a few kcal mol⁻¹ above the T_{1K} of 1 i.e. at 76 kcal mol⁻¹ (Fig. 5 and 6). The optimized structure of T_{1K} of 1 reveals that T_{1K} of 1 is at 68 kcal mol⁻¹ above its S₀, considerably lower than the energy obtained by the TD-DFT calculations. However, it should be noted that DFT/B3LYP optimization of the triplet ketones with (n,π^*) configuration underestimates their energy as reported earlier.^[22–26] Analysis of the calculated bond lengths in the T_{1K} of 1 shows indeed that the C=O bond is elongated in comparison to the calculated C=O bond length in its S_0 (Fig. 5), as was expected for triplet ketones with (n, π^*) configuration. Furthermore, the $C_\beta – C_\gamma$ bond length in the T_{1K} of 1 is similar to the one in its S_0 , thus demonstrating that T_{1K} of 1 is best described as



Scheme 2. Proposed mechanism for forming triplet biradical 2 from 1.



Fig. 5. Optimized conformers of 1, T_{1K} of 1, and biradical 2. The bond lengths are given in Å.



Fig. 6. Stationary points on the triplet energy surface of 1. Calculated energies are in kcal mol⁻¹. The energies were obtained from optimization of 1, T_{1K} of 1, and biradical 2. TD-DFT calculations were used to obtain the energies of S_{1K} , T_{1K} , and T_{2K} of 1 using the optimized structure of 1.

triplet acetophenones. The spin density calculation further supported this notion as the unpaired spin is localized on the carbonyl oxygen atom and the phenyl group of T_{1K} of **1** (Chart 3).

The optimization of triplet biradical **2** shows that it is located at 62 kcal mol⁻¹ above the S₀ of **1**, only a few kcal mol⁻¹ below the T_{1K} of **1**. The calculated C_β-C_γ bond length in **2** is 1.45 Å (Fig. 5), and thus it can be described as having single-bond character. The dihedral angle of H-C_β-C_γ-H in **2** is 92° to reduce the overlap between the two adjacent radical centres. Furthermore, the spin density calculation placed the unpaired electrons on the C_β and C_γ atoms, which have spin densities of 0.87 and 0.96, respectively, demonstrating that **2** is a 1,2-biradical with the two radical centres localized on the C_β and C_γ atoms (Chart 3).

The calculated rotational barrier for the biradical **2** around its C_{β} - C_{γ} bond is displayed in Fig. 7. The rotational calculations further support that biradical **2** is the most stable, as the two radical centres are almost perpendicular to each other. The calculated rotational barriers around the C_{β} - C_{γ} bond are significant at 16 and 15 kcal mol⁻¹.

The calculated stationary points on the triplet surface of 1 are shown in Fig. 6. The calculations show that an energy transfer from T_{1K} of 1 to form biradical 2 is feasible as the biradical 2 is several kcal mol⁻¹ lower in energy than the T_{1K} of 1.



Chart 3. Calculated spin densities for T_{1K} of 1 and triplet biradical 2.



Fig. 7. Calculated rotational barrier for **2**. Torsion angle is represented by the blue chemical bonds in the structure displayed in the upper left corner of the plot.



Scheme 3. Formation of biradical **3** from T_{1K} of **1** and calculated spin densities of biradical **3**.



Fig. 8. TD-DFT-Calculated spectrum for biradical 3 in acetonitrile.

Furthermore, the calculations also support the isoprene quenches T_{1K} of 1 efficiently as the energy of the triplet-excited state of isoprene is 60 kcal mol^{-1[27]} and thus lower than for T_{1K} of 1. Furthermore, isoprene is not expected to quench biradical 2 efficiently due to their similar energies.

We also calculated the triplet biradical formed by addition of T_{1K} of 1 to the vinyl bond to form biradicals 3 (Scheme 3). The optimized structure of biradical 3 is located 51 kcal mol⁻¹ above S_0 of 1, and the calculated spin density shows that one of the radical centres is localized on the carbon atom in the five-membered heterocyle, whereas the other radical centre is conjugated with the phenyl group. The transition state for forming biradical 3 from T_{1K} of 1 is located at 9 kcal mol⁻¹ above its optimized structure. The calculated TD-DFT spectrum of 3 is displayed in Fig. 8, and it does not match with the observed spectra in Figs 1 and 4, thus further supporting that biradical 3 is not formed upon irradiating 1.

Although biradical 3 is more stable than biradical 2, it is not formed upon irradiating 1 because energy transfer must be more efficient than T_{1K} of 1 rearranging into biradical 3. The transition state barrier for forming biradical 3 from T_{1K} of 1 is significant enough that it cannot compete with energy transfer to form biradical 2.

Phosphorescence

The phosphorescence spectrum of **1** was obtained at 77 K in frozen ethanol matrices (Fig. 9). The obtained phosphorescence spectrum of **1** has resolved the emission bands typically observed for ketones with (n,π^*) configurations. Furthermore, the first vibrational band at 391 nm was assigned to the (0,0) band of the phosphorescence, which corresponds to the energy of T_{1K} of **1** i.e. 73 kcal mol⁻¹. Therefore, the energy obtained for T_{1K} of **1** from the TD-DFT calculations is in excellent agreement with the experimental value (Table 1).

Product Studies

Photolysis of **1** in argon-saturated [D]chloroform through a Pyrex filter (>300 nm) at ambient temperature yielded no new products. The photolysis of **1** was monitored by ¹H NMR spectroscopy and gas chromatography mass spectrometry,



Fig. 9. Phosphorescence of 1 in ethanol at 77 K obtained upon 308-nm excitation.

Table 1. Comparison of the measured and calculated energies $(kcal mol^{-1})$ of T_{1K} and T_{2K} of 1

$\frac{Phosphorescence^{A}}{T_{1}}$	Optimization ^B T ₁	TD-DFT ^C	
		T ₁	T ₂
73	68	72	76

^AObtained from phosphorescence spectrum of 1; ^BObtained from optimization; and ^CObtained from TD-DFT calculations.

which showed that **1** does not form any photoproduct as expected. Furthermore, the irradiation of **1** in oxygen-saturated [D]chloroform also yielded no new products (Scheme 4), thereby confirming that biradical **2** is not trapped with oxygen to form new products.

We prepared 1 with a deuterium (d) substitution on the β -position (Scheme 4). Before photolysis, the ratio of the *trans*-1-d-to-*cis*-1-d was 47% according to ¹H NMR spectro-scopy. After 5 h of irradiation through Pyrex filter, the ratio of *trans*-1-to-*cis*-1 became 44%. Thus, verifying that 1 undergoes *cis*-*trans* isomerization upon irradiation.

Discussion

Laser flash photolysis demonstrated that irradiation of **1** leads to the formation of triplet biradical **2**, and the formation of biradical **2** is independent of irradiation wavelength. The photochemistry of **1** is not affected by the irradiation wavelength as the ketone chromophore absorbs more significantly than the alkene moiety at both 308 and 266 nm. In comparison, the photochemistry of α , β -vinylketones **4** is wavelength dependent because irradiation at a shorter wavelength selectively excited the vinylketone chromophore that did not undergo intersystem crossing to the triplet surface. In contrast, irradiating **4** at longer wavelengths resulted in the acetophenone chromophore to absorb light to form T_{1K} of **4**, which rearranged to biradical **5** (Scheme 5).

The energy transfer rate from T_{1K} of **1** to form biradical **2** is similar to the rate for T_{1K} of **4** to rearrange to form biradical **5**. Similarly, the lifetimes of triplet biradicals **2** and **5** are comparable, although the calculated rotational barrier for the *cis-trans* isomerization is considerably larger for biradical **2** than that for **5** i.e. ~16 and ~8 kcal mol⁻¹, respectively. However, because biradical **2** only needs to rotate into a conformation that is aligned for intersystem crossing to the singlet surface to form both *cis*-1 and *trans*-1, rather than undergoing *cis-trans* isomerization on the triplet surface, it is rational that the lifetimes of **2** and **5** are similar as they are both limited by intersystem crossing.

There is not a significant difference in the properties of biradicals 2 and 5. The resonance stabilization of the α -radical



Scheme 4. Product studies of 1.



Scheme 5. Proposed mechanism for the *cis-trans* isomerization of 4.

centre in biradical **5** does not affect its reactivity significantly in comparison to **2**.

Finally, we compared the reactivity of triplet biradical 2 with triplet 1,2-biradical 7, which is formed by intramolecular sensitization of vinylazide 6 (Scheme 6).^[17] The major difference between biradical 7 and biradicals 2 and 5 is that biradical 7 decays by extruding a nitrogen molecule to form triplet vinylnitrene 8 rather than undergoing intersystem crossing to reform vinylazides 6. Triplet biradical 7 has a lifetime of 2.4 µs at ambient temperature in acetonitrile, which is on the same order as the lifetimes observed for biradicals 2 and 5. Thus, the only significant difference between among 7, 2 and 5 is that it was possible to measure the rate of reaction biradicals 7 and 5 with oxygen, whereas for biradical 2, the transient absorption is fully quenched in oxygen. It can be theorized that triplet biradicals 7 and 5 react slower with oxygen than biradical 2 because they have an electron-withdrawing azido and carbonyl groups, respectively. Several research scientists have studied the reactivity of oxygen with alkyl- and hydroxyalkyl radicals in the gas phase and have shown that there is a correlation between the ionization potentials of these radicals and their rate of reaction with oxygen.^[28-30] However, it is possible that T_{1K} of 2 more efficiently quenched with oxygen than T_{1K} of **6**.

Conclusion

We have demonstrated that triplet sensitization of simple alkenes results in formation of 1,2-biradical, which has a lifetime of a few microseconds and intersystem crosses to reform its ground state. Thus, the intramolecular sensitization of unconjugated alkenes is an efficient method of forming 1,2-biradicals, and it can potentially be used for *cis-trans* isomerization of simple alkenes in applications.

Experimental

Calculations

All geometries were optimized using *Gaussian09* at B3LYP level of theory and 6-31G+(d) basis set.^[19,20,31] The UV absorption spectra were calculated using the TD-DFT.^[31-34] The self-consistent reaction field method with the integral equation formalism polarization continuum model with acetonitrile as solvent were used to calculate the effect of solvation.^[35-38]

Laser Flash Photolysis

The laser flash photolysis was performed with an Excimer laser (308 nm, 17 ns, 105 mJ) and Nd:YAG laser (266 nm, 2 ns,

145 mJ).^[16] A stock solution of 1 in spectroscopic grade acetonitrile was prepared such that the solutions displayed absorption between 0.3 and 0.6 at 308-nm excitation wavelength. In a typical experiment, the stock solution ($\sim 1 \text{ mL}$) was placed in a 10 mm \times 10 mm wide and 48 mm long, quartz cuvette and was purged with argon or oxygen for 5 min. The rate constants were obtained by fitting on average three-to-five kinetic traces.

Phosphorescence

A 5 mM ethanol solution of 2-methyl-1-phenylbut-3-en-1-one (1) was prepared, and its phosphorescence spectra was obtained at 77 K (Horiba instruments Inc., Edison, NJ, USA; Horiba Jobin-Yvon fluorolog with 5 nm as the emission monochromator bandwidth). The solutions were irradiated at 308 and 266 nm, and the emission spectra were recorded in the range of 300–800 nm.

Preparations of Starting Materials

Synthesis of 2-methyl-1-phenylbut-3-en-1-ol

2-Methyl-1-phenylbut-3-en-1-ol was synthesized following a modified procedure based on the method used by Imai and Nishida.^[39] Benzaldehyde (5.3 g, 50 mmol) was dissolved in dimethylformamide (100 mL). To the magnetically stirred solution, crotyl chloride (5.0 g, 55 mmol, 1.1 equiv.) and SnCl₂·H₂O (17.0 g, 75 mmol, 1.5 equiv.) were added. NaI (11.2 g, 75 mmol, 1.5 equiv.) was added slowly over a period of 10 min, and a mild exothermic reaction was noted at the early stage. After stirring for 20 h at room temperature, 30 % aqueous NH₄F (100 mL) and diethyl ether (Et₂O; 200 mL) were added. The mixture was stirred for an additional 30 min. The ether layer was extracted and washed twice with water (100 mL) and saturated aqueous NaCl solution (100 mL). The ether laver was dried over anhydrous MgSO₄ and evaporated under reduced pressure to get a clear oil of 2-methyl-1-phenylbut-3-en-1-ol (7.5 g, 46 mmol, 93 %). v_{max} (neat)/cm⁻¹ 3439br (OH). The ¹H NMR and IR spectra matched those reported in the literature.^[40] δ_H (CDCl₃, 400 MHz) 0.88 (3H, d, J 8.0), 1.02 (2H, d, J 8.0), 2.17 (1H, br s), 2.51-2.41 (1H, m), 2.66-2.56 (1H, m), 4.37 (1H, d, J 8.0), 4.61 (1H, d, J 4.5), 5.08-5.03 (2H, m), 5.17-5.23 (2H, m), 5.72-5.86 (2H, m), 7.39-7.24 (10H, m).

Synthesis of 2-methyl-1-phenylbut-3-en-1-one (1)

The procedure reported by Ranaweera et al.^[11] was followed with some minor modifications. The Jones reagent was prepared by dissolving CrO₃ (10 g) in H₂SO₄ (10 mL) and water (30 mL). A stirred slurry of 2-methyl-1-phenylbut-3-en-1-ol (7.0 g, 43 mmol) in acetone (100 mL) at 0°C was added until the color of Jones reagent changed to orange yellowish. The solution was filtered, the solvent was removed under reduced pressure, and the residue was dissolved in Et₂O (200 mL). The ether layer was washed with water (100 mL) and saturated aqueous NaHCO₃ and dried over MgSO₄. Removal of the solvent under vacuum produced a crude 2-methyl-1-phenylbut-3-en-1-one. The



Scheme 6. Formation of triplet vinylnitrene through 1,2-biradical 6.

residue was purified on a silica column eluted with ethyl acetate/ hexane (3 : 7) to yield 1 as a clear oil (5.8 g, 36 mmol, 83 %). ν_{max} (neat)/cm⁻¹ 3060, 2978, 2933, 1684 (C=O), 1596, 1448, 1215, 962, 702. The ¹H NMR, ¹³C NMR, and IR spectra matched the those reported in the literature.^[40] $\delta_{\rm H}$ (CDCl₃, 400 MHz) 1.35 (3H, d, *J* 6.8), 4.19 (1H, dq, *J* 6.8, 7.6), 5.15 (1H, d, *J* 10.2), 5.20 (1H, d, *J* 17.3), 6.01 (1H, ddd, *J* 7.6, 10.2, 17.3), 7.49 (2H, m), 7.58–7.54 (1H, m), 7.99 (2H, d, *J* 7.0). $\delta_{\rm C}$ (CDCl₃, 100 MHz) 201.1, 138.2, 136.3, 132.9, 128.5, 128.4, 116.5, 45.5, 17.0. *m/z* (electron impact) 160 (M⁺).

Photolysis of 2-methyl-1-phenylbut-3-en-1-one (1)

Product Studies of 1 in Argon or Oxygen-Saturated CDCl₃

A solution of 1 (15 mg, 93 μ mol) in CDCl₃ (2 mL) was purged with argon or oxygen for 5 min and photolyzed through a Pyrex filter at ambient temperature. The ¹H NMR spectrum of the irradiated solution was recorded every 30 min during the 3-h irradiation period, and no significant changes were observed in the ¹H NMR spectra.

Supplementary Material

Cartesian coordinates and energies of **1** and NMR and IR spectra of **1**; synthesis and ¹H NMR spectra of **1**-d are available from the Journal's website.

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