Photochemical C−C Bond Cleavage of 1,2-Diarylcyclopropanes Bearing an Acetylphenyl Group. Generation and Observation of Triplet 1,3-Biradicals

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The photochemical properties of 1,2-diarylcyclopropanes bearing an acetylphenyl group were studied by product analysis and laser flash photolysis. All cyclopropanes showed efficient cis−trans photoisomerization followed by inefficient isomerization to 1,3-diarylpropenes. All the products were unquenched by the addition of triplet quencher, 2-methyl-1,3-butadiene ($E_T \simeq 60$ kcal mol^{-1}), whereas molecular dioxygen gave oxygenated products. Triplet 1,3-biradicals generated from a short-lived acetophenone-like triplet ($\lesssim$1 ns) were observed as intermediates in these reactions through nanosecond laser flash photolysis. Polar substituent effects on the lifetime of the 1,3-biradicals were small, except for a heavy atom effect in the case of Br. Spin−orbit coupling calculations on model 1,3-biradicals show a negligible effect on polar substituent and thus predict a negligible effect on the intersystem crossing rate. Conjugated biradicals in general now seem unlikely to show the "ionic character effect" on intersystem crossing suggested by the work of Salem and Rowland.

Introduction

Biradicals are among the most important intermediates in solution phase organic chemistry. The chemical behavior of biradicals (i.e., products and respective ratios) is strongly dependent upon spin multiplicity. Thermally produced singlet biradicals decay to ground state products too rapidly to be detected with spectroscopic techniques. Triplet biradicals, produced from excited triplet state precursors, cannot decay directly to the ground state since this process would be spin-forbidden. They must convert to singlet biradicals via intersystem crossing (isc) before yielding final products. The lifetime, τ, of a triplet biradical is normally expressed as

$$\tau = (k_{\mathrm{isc}})^{-1}$$

where k_{isc} is the rate of intersystem crossing and is determined by the magnitude of spin−orbit coupling (SOC) between the singlet (S) and the triplet (T) states.[1] The lifetimes of typical triplet biradicals, measured either by laser flash photolysis[2,3] or through kinetic studies,[4] are of nanosecond order (1−900 ns). Spin−orbit coupling is increased by (1) minimized distance between the termini; (2) perpendicular yet overlapping p orbital orientation; and (3) ionic character in the S wave function.[1] For short-chain biradicals, the SOC mechanism will dominate because of the closeness of the termini. For hexamethylenes and longer chain biradicals, however, hyperfine coupling (HFC) dominates in isc for extended conformations,[5−8] since SOC decreases exponentially with an increase in the inter terminal distance and HFC interaction is distance independent.

After the first flash spectroscopic detection of 1,4-biradical intermediates in the Norrish type II reaction by Scaiano in 1977,[9,10] several biradicals, including longer chain species produced by the Norrish type I reaction, have been detected by laser flash photolysis.[2,3] The lifetimes of 1,n-biradicals have been compared as a function of either n,[11−15] or the distance between the termini.[16,17] These results have qualitatively supported the distance dependence predicted by Salem and Row-

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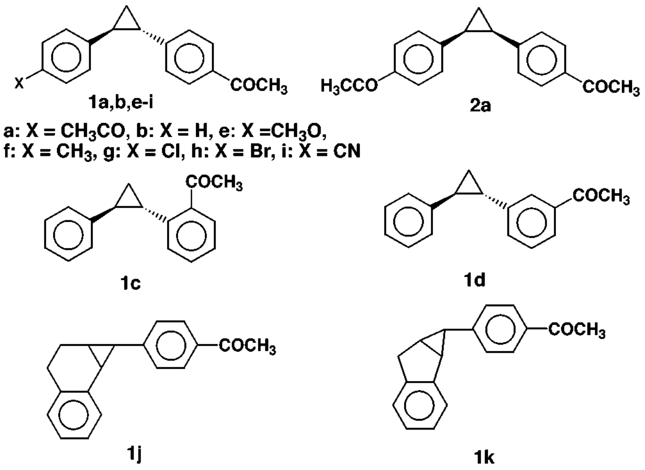

Figure 1. The 1,2-diarylcyclopropanes investigated in this work.

land. Trimethylene, a proposed intermediate in the isomerization of cyclopropane derivatives,[18–25] has long been a model for theoretical studies of intersystem crossing[16,26,27] since, with the exception of carbenes and excited alkenes, trimethylene is the smallest biradical. Although lifetimes for 1,3-cyclopentanediyls[28,29] were known, lifetimes of flexible 1,3-biradicals in room-temperature solution, though desired,[30,31] were not available until 1985, when we first reported the measurement of 1,3-biradical lifetimes.[32]

In this paper, we report substituent and conformational effects on the photochemistry of 1,2-diarylcyclopropanes bearing acetylphenyl groups and related compounds (**1a**−**k**). These compounds are shown in Figure 1. We show the intermediacy of triplet 1,3-biradicals in their geometric photoisomerization and determine the lifetimes of the corresponding 1,3-biradicals by laser flash photolysis. Since excitation of the acetylphenyl group will produce the excited triplet state by rapid intersystem crossing from the excited singlet state, we expected intramolecular sensitization by the acetophenone chromophore, leading to efficient generation of triplet 1,3-biradicals, thus avoiding the operational difficulty of an external sensitizer.

Scheme 1

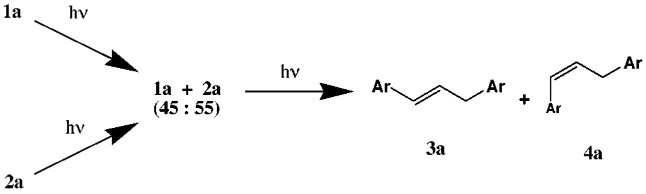

Table 1. Quantum Yields for the Formation of Photoproducts in the Photoisomerization in Benzene at 18 °C[a]

reaction	Φ^b
1a → **2a**	0.45 ± 0.02
2a → **1a**	0.11 ± 0.02
1a or **2a** → **3a** + **4a**	0.005

[a] [**1a**] = [**2a**] = 1.0×10^{-2} mol L^{-1}. [b] Values for 313 nm light. Determined by HPLC.

Table 2. Quantum Yields for the Formation of 2a in the Photoisomerization of 1a at Various Concentrations of 1a in Benzene at 18 °C

concn, mol L^{-1}	$\Phi_{1a\to 2a}{}^a$
1.0×10^{-3}	0.51 ± 0.04
5.0×10^{-3}	0.46 ± 0.02
1.0×10^{-2}	0.45 ± 0.02
2.5×10^{-2}	0.47 ± 0.02

[a] Values for 313 nm light. Determined by HPLC.

Results and Discussion

Stationary State Photochemistry of 1,2-Diarylcyclopropanes Bearing an Acetylphenyl Group. Irradiation of a benzene solution containing *trans*-1,2-bis(4-acetylphenyl)cyclopropane (**1a**) with 313 nm light caused efficient cis−trans isomerization of the cyclopropane and gave a mixture of *cis*- and *trans*-cyclopropanes in a ratio of 55:45 (±1) within 1 h (Scheme 1). On prolonged irradiation (54 h) the cyclopropanes gradually isomerized to (*E*)- and (*Z*)-1,3-bis(4-acetylphenyl)propene (*E*-**3a** and *Z*-**4a**, *E*/*Z* = 2/1) which were isolated in 42% yield. ^{1}H NMR and HPLC analyses of this photoreaction revealed that **3a** and **4a** were primary products which were formed even in the early stages of the reaction; however, the efficiency for formation of **3a** and **4a** was quite low. Similarly, **2a** also isomerized to give a mixture of **1a**, **3a**, and **4a** upon irradiation. Irradiation of a mixture of **3a** and **4a** did not yield **1a** and **2a**. Irradiation of **1a** or **2a** in methanol gave their isomers **1a**, **2a**, **3a**, and **4a**. No polar addition products were obtained.[33,34] This result excludes the intermediacy of ionic species in the isomerization. Moreover, irradiation in the presence of 2-propanol or in the presence of 1.0 M ethanethiol in benzene did not cause the reduction of the acetyl group to a 1-hydroxyethyl group. Quantum yields for these photoreactions in benzene were measured in both the absence and presence of additives (Tables 1−3). The difference between $\Phi_{c\to t}$ and $\Phi_{t\to c}$ may be explained by energy wastage. Differential yields of transients are inconsistent with results from transient spectra which

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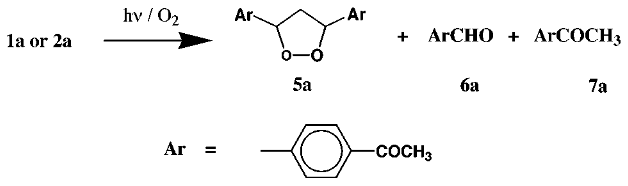
Table 3. Quantum Yields for the Formation of 2a in the Presence of Triplet Quencher in Benzene at 18 °C[a]

quencher	concn, mol L^{-1}	$\Phi_{1a\rightarrow 2a}$[b]
2-methyl-1,3-butadiene	0.05	0.49 ± 0.04
	0.42	0.57 ±0.05
	2.82	0.45 ±0.06
oxygen	saturated	0.53 ± 0.04

[a] [**1a**] = 1.0×10^{-2} mol L^{-1}. [b] Values for 313 nm light. Determined by HPLC.

Scheme 2



show identical transient intensity from matched optical densities of 90:10 cis/trans mixtures. Quantum yield discrepancies are under further investigation. The quantum yield for the cis−trans isomerization was not dependent on the concentration of **1a**. The addition of a triplet quencher, 2-methyl-1,3-butadiene (isoprene), did not affect the isomerization. The above behavior may suggest the incorporation of singlet intermediates in these photoreactions; however, irradiation of **1a** in benzene with vigorous bubbling of oxygen afforded a mixture of 3,5-bis(4-acetylphenyl)-1,2-dioxolane (**5a**), 4-acetylbenzaldehyde (**6a**), and 1,4-diacetylbenzene (**7a**) in a 1:1:1 ratio (Scheme 2). The structure of **5a** was assigned by the ^{1}H NMR spectrum and the chemical conversions.[35] Either irradiation or heating to 150 °C of a mixture of **5a**, **6a**, and **7a** quantitatively afforded **6a** and **7a** in a 1:1 mixture. Whereas direct irradiation of 1,2-bis(4-methoxyphenyl)cyclopropane did not yield oxygenation products, but rather caused the cis−trans isomerization although 9,10-dicyanoanthracene-sensitized photoxygenation of this compound efficiently gave 3,5-bis(4-methoxyphenyl)-1,2-dioxolanes.[35] These results suggest the intermediacy of a triplet 1,3-biradical in the photoisomerization of **1a** and **2a**, although irradiation of **1a** in the presence of an alkene, such as methyl acrylate or butyl vinyl ether (0.5 mol L^{-1}), did not produce any products other than **2a**, **3a**, and **4a**.

Various sensitizers were employed to effect the triplet photosensitization of the cis−trans isomerization of **1a** to **2a**. The isomerization sensitized by acetophenone, which is the same chromophore contained in **1a**, was as efficient as that of direct irradiation. However, when sensitzers with lower triplet energy were employed, the quantum yield for the isomerization decreased (Table 4). These results strongly suggest that the cis−trans isomerization proceeds from an acetophenone-like triplet ($E_T \simeq$ 72 kcal mol^{-1}).

Table 4. Quantum Yield for the Formation of 2a in the Aromatic Ketone-Sensitized Photoisomerization of 1a in Benzene[a]

aromatic ketone (E_T, kcal mol^{-1})	concn/mol L^{-1}	$\Phi_{1a\rightarrow 2a}$[b]
acetophenone (73.7)	0.036	0.41 ± 0.02
	0.32	0.44 ± 0.02
	1.01[c]	0.39 ± 0.02
benzophenone (68.6)	0.40[c]	0.39 ± 0.02
benzil (53.4)	0.04[c]	0.07 ± 0.03

[a] [**1a**] = 1.0×10^{-2} mol L^{-1}. [b] Values for 313 nm light. [c] >90% of 313 nm light was absorbed by the sensitizer.

Table 5. Quantum Yields for the Formation of 2b−d in the Photoisomerization of 1b−d in Benzene in the Absence and Presence of 2-Methyl-1,3-butadiene

compound	[2-methyl-1,3-butadiene], mol L^{-1}	$\Phi_{1\rightarrow 2}$[a]
1b[b]	0	0.38 ± 0.03
	0.515	0.38 ± 0.03
	0.784	0.33 ± 0.03
1c[c]	0	0.20 ± 0.02
	0.140	0.23 ± 0.02
	0.235	0.21 ± 0.02
	0.456	0.24 ± 0.02
1d[d]	0	0.45 ± 0.03
	0.226	0.39 ± 0.03
	0.434	0.39 ± 0.03
	0.754	0.31 ± 0.02

[a] Values for 313 nm light. Determined by GLC. [b] [**1b**] = 4.78×10^{-3} mol L^{-1}. [c] [**1c**] = 5.19×10^{-3} mol L^{-1}. [d] [**1d**] = 4.25×10^{-3} mol L^{-1}.

Table 6. Properties of Transient Species

compound	solvent	lifetime, ns	λ_{max}, nm	ref
1a	MeOH	13.4 ± 1	327	*c*
	Heptane	14.7 ± 1	320	*c*
2a	MeOH	13.0 ± 1	327	*c*
1b	Heptane	15.1 ± 1	311	*c*
acetophenone	Benzene	3000		38
	EtOH	140	270	38
4-methylacetophenone	cyclohexane		340	39
3a/**4a**[a]	MeOH	29 ± 1	320	*c*
(*E*)-AnCH=CHCH$_2$Ph[b]	MeOH	34 ± 1		41
(*E*)-PhCH=CDCH$_2$Ph	MeOH	33		41
PhCH$_2$	EPA[d]		319	37
PhC(OH)CH$_3$	cyclohexane		370	39
	EtOH		330	38

[a] (**3a**/**4a** = 2/1). [b] An = anisyl = 4-MeOC$_6$H$_4$. [c] This work. [d] Ether−isopentane−EtOH glass at 77 K.

The irradiation (313 nm) of *trans*-1-(4-acetylphenyl)-2-phenylcyclopropane (**1b**) in benzene rapidly afforded the cis isomer **2b**. The ratio of **1b** to **2b** reached a photostationary state of 45:55 (±1). They afforded a mixture of four isomeric 1,3-diarylpropenes upon prolonged irradiation. These alkenes were also formed as primary products. The photoreaction was not quenched by the addition of 2-methyl-1,3-butadiene (0.5 mol L^{-1}). Similarly *trans*-1-(2-acetylphenyl)-2-phenylcyclopropane (**1c**) and *trans*-1-(3-acetylphenyl)-2-phenylcyclopropane (**1d**) isomerized and afforded photostationary mixtures of cis and trans isomers in ratios of 62:38 and 44:56 (±1), respectively. The addition of 2-methyl-1,3-butadiene did not affect the photoisomerization of **1c** to **2c**, but did slightly affect that of **1d**. Quenching by 2-methyl-1,3-butadiene may suggest the incorporation of a locally excited acetophenone-like triplet precursor in the photoisomerization. The quantum yields for the photoisomerization of **1b**−**d** to **2b**−**d** in the absence and presence of 2-methyl-1,3-butadiene are summarized in Table 5. Efficient cis−trans isomerization of 1-(4-acetylphenyl)-2-(4-substituted phenyl)cyclopropanes (**1e**−**i**) was also observed by irradiation (313 nm) in benzene with no substantial substituent effect observed (Table 7).

Laser Flash Spectroscopy. Laser flash photolysis of a heptane solution of **1a** (fourth harmonic of Nd:YAG laser, 266 nm, fwhm 1.75 ns, unfocused ca. 20 mJ/pulse) produced a transient with an absorption maximum, λ_{max}, at 320 nm and a lifetime of 14.7 ± 1 ns. A similar

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Table 7. Substituent Effects on the Photoisomerization of *trans*-1-(4-Acetylphenyl)-2-(4-substituted phenyl)cyclopropanes (1a–b, 1e–i) and the Lifetime of the Corresponding 1,3-Biradicals

compound	X	$\Phi_{1\to 2}{}^{a}$	$\lambda_{max}{}^{b}$	lifetime/ns
1a	CH_3CO	0.45	320	14.7 ± 1.0
1b	H	0.38	311	15.1 ±1.0
1e	CH_3O	0.19	315	14.5 ± 0.5
1f	CH_3	0.51	310	14.0 ± 0.2
1g	Cl	0.58	310	13.1 ± 0.6
1h	Br	0.57		5.2 ± 0.4
1i	CN	0.40	305	16.0 ± 0.5

[a] Values for 313 nm light. Determined by GLC. [**1**] = 5 × 10^{-3} mol L^{-1}. [b] Values in heptane.

transient absorption (λ_{max} = 320 nm, τ = 13.4 ±1 ns) was observed for a methanol solution of **1a**. These signals were unaffected by the addition of 2-methyl-1,3-butadiene (1 mol L^{-1}) in either their intensity, lifetime, or λ_{max}. Oxygen saturation of an acetonitrile solution of **1a** shortened the lifetime from 15.7 ± 0.2 to 7.1 ± 0.5 ns. The transient spectroscopic study of **2a** also showed strong signals identical in lifetime, absorption maxima, and changes in optical density, ΔOD, to those observed for **1a**. These transient signals were assigned to a triplet 1,3-biradical (^{3}**BR**) for the following reasons: (1) Due to the very fast intersystem crossing rate observed for the acetophenone chromophore (10^{10}–10^{11} s^{-1}),[17] the spin multiplicity of these signals were assigned as triplet. (2) The absence of quenching by 2-methyl-1,3-butadiene rules out the spectroscopic states ^{3}**1a*** and ^{3}**2a*** which, like triplet acetophenone, should be quenched at a diffusion-controlled rate.[36] (3) The absorption maxima are in accord with that of a benzyl radical,[37] not with that of a ketyl radical.[38,39] (4) The fact that excitation of **1a** and **2a** produces identical transients indicates that the transient is a stereorandomized species. (5) The transient is not the triplet of **3a** or **4a**, ^{3}**3a*** and ^{3}**4a***, since the transient observed by the irradiation of a mixture of **3a** and **4a** in methanol had both a different lifetime, τ = 29 ± 1 ns, and a different absorption maximum, λ_{max} = 310 nm. The lifetime agrees well with values reported for 1,3-diarylpropene triplets in methanol.[40,41] (6) The lifetime of the transient generated from **1a** did not show any appreciable temperature effect (E_a = 0.14 ± 0.1 kcal mol^{-1}). The absence of the acetophenone-like triplet precursors of the ^{3}**BR**, ^{3}**1a***, and ^{3}**2a*** in the laser flash photolysis study can be explained by their extremely short lifetimes. Similar results were obtained for *trans*-1-(4-acetylphenyl)-2-phenylcyclopropane (**1b**). The laser flash photolysis of **1b** produced a transient which was also assigned to the corresponding 1,3-biradical (τ = 15.1 ± 1 ns, λ_{max} = 311 nm in heptane). This transient was also unaffected by the addition of 2-methyl-1,3-butadiene (1 mol L^{-1}). *trans*-1,2-Bis(4-methoxyphenyl)cyclopropane, which isomerizes to the cis isomer upon direct excitation, afforded only a modest fluorescence and no observable absorption. The lifetimes and λ_{max} of the transient species generated from the excitation of **1a**, **2a**, and related compounds are listed in Table 6. The lifetime and λ_{max} of these species is in good agreement with those reported for the triplet 1,3-diphenyltrimethylene biradical.[42] The spectral broadness exhibited by these compounds was also observed for 1,3-diaryl-1,3-cyclopentanediyl triplet biradicals.[43,44] Figures 2 and 3 illustrate typical spectra and kinetic decay curves for these compounds.

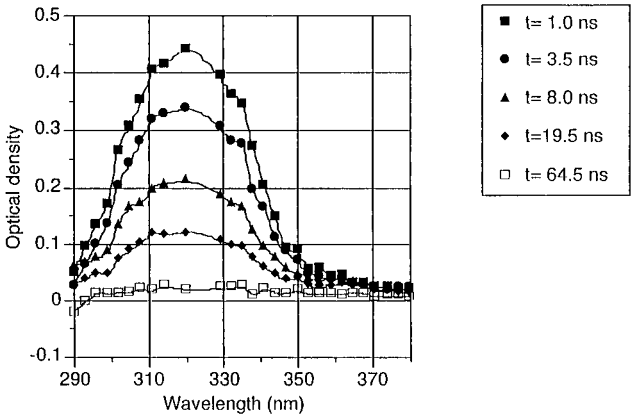

Figure 2. Transient absorption spectrum of compound **1j** in heptane: 266 nm excitation, 12 mJ/P, λ_{max} = 320 nm.

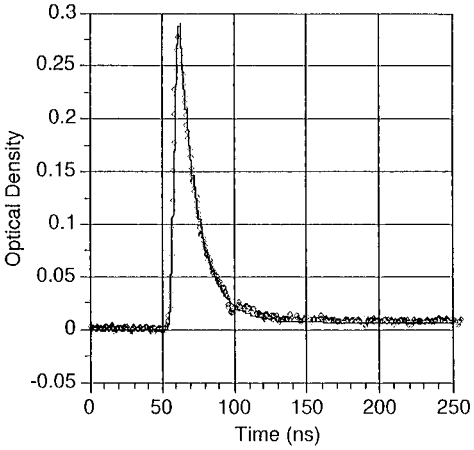

Figure 3. Transient decay curve of compound **1j** in heptane: 266 nm excitation, 12 mJ/P, monitored wavelength = 330 nm, τ = 12.9 ns.

An increase in isc rate generated by an increase in the ionic character of the termini within a biradical was predicted by Salem and Rowland.[1] To examine this proposed effect, a laser flash photolysis study of 1-(4-acetylphenyl)-2-(4-substituted phenyl)cyclopropanes (**1e–i**) was conducted. These compounds also showed transients which were assigned to the corresponding 1,3-biradicals. With the exception of 1-(4-acetylphenyl)-2-(4-bromophenyl)cyclopropane (**1h**), which produced a short-lived transient due most likely to the heavy atom effect,[15,28,29,45] these cyclopropanes produced transients with similar lifetimes and absorption maxima. These results are summarized in Table 7 which also includes quantum yields measured for the trans–cis photoisomerization.

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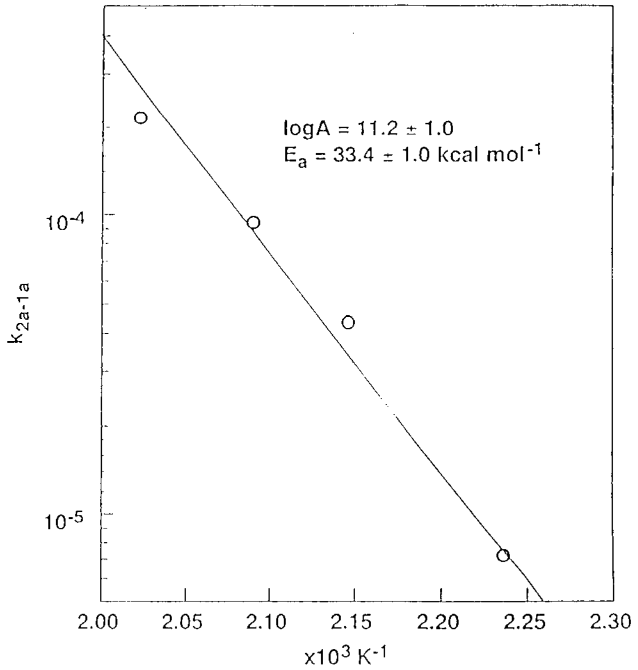


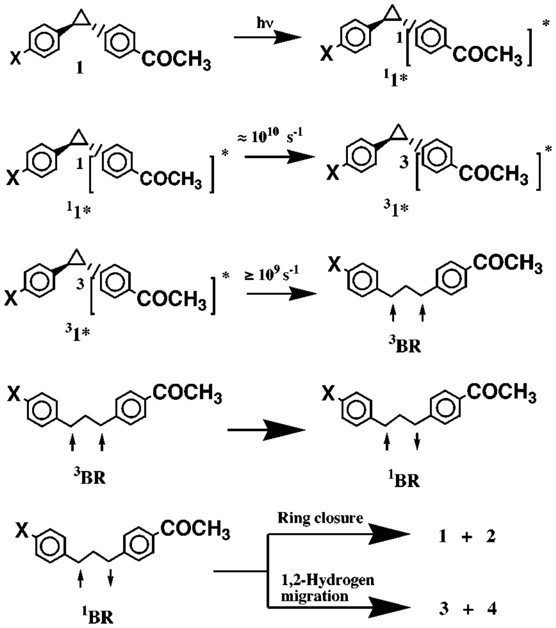
Figure 4. Arrhenius plot for thermal isomerization of **2a** to **1a**.

Conformational effects on the lifetime of 1,3-biradicals were examined through the use of a series of sterically restricted precursors, **1j**–**k**. Ring opening of **1j**–**k** will yield 1,3-biradicals where the intramolecular rotation of one radical terminal is limited so that the two p orbitals at the termini will have a nearly perpendicular configuration. Intramolecular rotation will be allowed for only one terminal; the other terminal will remain fixed. This arrangement will allow conformational effects to be probed.[1] Upon laser flash photolysis, these compounds also showed efficient generation of transients assigned as 1,3-biradicals. Compounds **1j**–**k** did not show any considerable photoisomerization, probably due to the instability of the cis isomers. The lifetimes were slightly shorter (14 and 12 ns for **1j** and **1k**, respectively) than that generated from **1a** or **1b**.

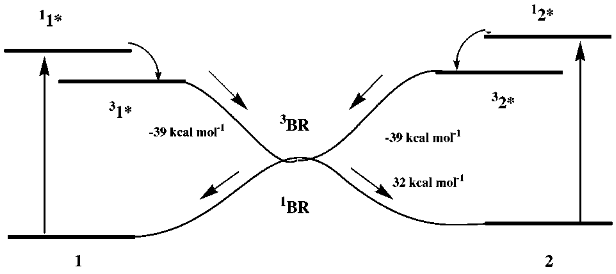
Thermal Isomerization of 1,2-Bis(4-acetylphenyl)-cyclopropane. As described above, the photoisomerization of 1,2-diarylcyclopropanes bearing an acetylphenyl group proceeds via the corresponding triplet biradicals. It has been proposed that thermal isomerization of cyclopropane derivatives also proceeds via a biradical mechanism. In this section, the thermal isomerization of **2a** to **1a** was studied to evaluate the energy surface of the reaction via the singlet biradical.

The thermal isomerization of **2a** to **1a** was observed by heating a diethylene glycol solution containing **2a** at 193 °C for 2 h. The photoisomerization products, **3a** and **4a**, were not observed. From the first-order plot of the isomerization reaction, the rate constant for isomerization was estimated as 4.33×10^{-5} s^{-1}. Rate constants were measured at ambient temperature. The activation parameters for the thermal isomerization of **2a** to **1a** were obtained from an Arrhenius plot of the rate constants (Figure 4) where $\Delta H = 33.4 \pm 1$ kcal mol^{-1} and log $A = 11.2$. These values are in accord with the reported values for 1,2-diarylcyclopropanes.[46]

Scheme 3



Scheme 4



Mechanism. Acetophenone derivatives typically have triplet energies of 72–74 kcal mol^{-1}. Because the compounds, **1a**–**k** and **2a**, all have either one or two acetylphenyl groups at vicinal positions, the triplet energies for these compounds are expected to be within this range. The excited triplet of acetophenone is quenched by conjugated dienes such as 2-methyl-1,3-butadiene ($E_T = 60$ kcal mol^{-1}) which in benzene quenches the acetophenone triplet at an almost diffusion controlled rate ($k_q = 5 \times 10^9$ mol^{-1} s^{-1}).[47]

A plausible mechanism for the photoisomerization of **1** and **2** is shown in Schemes 3 and 4. The first step is excitation of the acetylphenyl group, giving ^{1}**1*** (or ^{1}**2***) most probably in the ^{1}n,π* state, followed by rapid intersystem crossing (10^{10}–10^{11} s^{-1}) and internal conversion to the lowest triplet of the acetylphenyl group, ^{3}**1***. The absence of quenching of this triplet state by 2-methyl-1,3-butadiene and nonphosphorescent nature of **1** (or **2**) are due to the extremely short lifetime of ^{3}**1***. In the case of **1d**, the quenching coefficient, $k_q\tau$, was ca. 0.5, giving the lifetime of ^{3}**1d*** as 0.1 ns. The other cyclopropanes did not show considerable quenching, and therefore the lifetime of ^{3}**1*** will be less than 0.1 ns. This value is too short to detect with our present system for laser flash photolysis. The cyclopropane ring of ^{3}**1*** rapidly opens to give the 1,3-biradical (**BR**). In the triplet-sensitized photoreaction of **1a**, a decrease in the

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triplet energy of the sensitizer lowered the efficiency of isomerization. This indicates that the ring opening of **1a** requires excitation of the acetylphenyl group and illustrates the absence of nonvertical excitation to the biradical state. The spin multiplicity of the biradical was assigned as triplet (^{3}**BR**) on the basis of the results of dioxygen trapping and from the generation process.

Energy Correlation. The C−C bond cleavage of 4-alkylacetophenones from the $^3\pi,\pi^*$ state is symmetrically allowed, but forbidden from the ^{3}n,π^* state because a spin on the n orbital in the ^{3}n,π^* state will be conserved through the bond cleavage leading to a very high energy species in the latter case.[48] Even if the reaction originated in the lowest ^{3}n,π^* state of an acetophenone chromophore, the C−C bond stretching will couple best to the $^3\pi,\pi^*$ state. The reaction would then simply involve a surface crossing to the latter, which will be lower energy in the transition state region in any case. Cleavage of the C−C bond (normal bonds ca. 85 kcal mol^{-1}) will be facilitated by the generation of two benzylic radical sites (12.5 × 2 kcal mol^{-1}) and by the strain relief resulting from opening the cyclopropane ring (27 kcal mol^{-1}). The estimated triplet energy of these compounds is 72 kcal mol^{-1}. Thus, the energy change for the bond cleavage from the excited triplet state will be negative: $(85 - 72 - 12.5 \times 2 - 27) = -39$ kcal mol^{-1}. We neglect the small effect of the two aryl substituents. The resultant radical sites have been predicted to contain no strain energy.[49]

Fate of ^{3}BR. After intersystem crossing from ^{3}**BR** to ^{1}**BR**, ring closure occurs, with the biradical isomerizing to **1** or **2** and **3** or **4**. For simple trimethylene derivatives, this process tends to lead to the formation of cyclopropane, yielding less olefin.[50] In the present work, the quantum yield for the formation of **3** and **4** is also much smaller than that of cis−trans isomerization, though chemical yield is considerably high. This can be explained by repetitive excitation of **1a** and **2a**; the triplet olefin has no path for hydrogen migration as that which is known for the excited singlet 1,3-diphenylpropene derivatives.[51] The absence of **3a** or **4a** upon thermolysis of **2a** also supports the conclusion that the energy surfaces of the present 1,3-diaryl-substituted 1,3-biradicals are similar to those of the simpler trimethylene.

A few examples of substituent effect on the lifetime of 1,4-biradicals have been reported for Norrish II biradicals and photoenols. A substituent effect for 1,3-biradicals bearing a 4-substituted phenyl group, with the exception of a heavy atom effect by the 4-Br group, was not observed in this work. This suggests that any polar effect induced by the substituents does not affect the intersystem crossing rates of the present 1,3-biradicals; rather, the interaction between the two termini may be dominant due to their relative closeness. The heavy atom effect showed that considerable spin density is present at the 4-position of the phenyl ring.

The lack of any observed conformational effect in the 1,3-biradicals obtained from **1j**−**k** also illustrates the importance of the closeness between the two termini in intersystem crossing. Since the orientational factor for mutual interaction between termini in 1,3-biradicals is determined only by two rotational angles, through-bond interaction must be a dominant factor in the isc mechanism rather than through-space interaction. We also have observed a lack of conformational effect in the isc rate between sterically restricted and unrestricted 1,4-biradicals.[3,17,45,52,53] This observation will be discussed in a separate paper.

Computation of Spin−Orbit Coupling Constants for Model Trimethylenes. In view of the virtual absence of a polar substituent effect on the isc rate of the triplet biradicals, we calculated spin−orbit coupling constants (SOCC) for 1-amino-3-cyanotrimethylene and, for comparison, unsubstituted trimethylene. Spin−orbit coupling in biradicals is expected[1] to depend on the “ionic character in the singlet wave function,” by which is meant the fractional contribution of the VB hole−pair configuration.[54] If the anticipated effect of ionic character in the singlet biradical wave function were ever to be manifested in a study of polar substituents, surely 1-amino-3-cyanotrimethylene would be among the best examples. The absence of a polar substituent effect for the isc rate of the diaryl-1,3-propanediyls here reported is in complete accord with the outcome of our computations. We also performed analogous computations for (aminomethyl)borane, $H_2NCH_2BH_2$. The singlet in this case will be essentially a pure hole−pair state, the “hole” on the boron and the lone pair of electrons on the nitrogen, since that form is in fact the one with zero formal charge on all atoms. The triplet would necessarily be of the “dot-dot” type (one electron mainly on B and one on N). Clearly the “ionic character in the singlet wave function” will be maximized for such a case, completely analogously to the perpendicular aminoborane case described by Michl and Bonacic-Koutecky,[54] and this system will show the maximum SOCC to be expected for a trimethylene analogue in the absence of heavy atom effects.

We used the 2-in-2 CAS-MCSCF protocol and the spin−orbit coupling program of Furlani and King[55] with the 3-21G basis set as we have previously described.[56,57] For 1-amino-3-cyanotrimethylene and trimethylene, the C1−C2 and C2−C3 distances were taken as 1.502 Å, the sp^2 C−H bond distances were 1.07 Å, the sp^3 C−H bond distances were 1.09 Å, the bond angles at C1 and C3 were taken as 120°, and the bond angles at C2 were taken as tetrahedral (109.5°). For the amino group, the C1−N distance was 1.36 Å, the N−H distances were 0.96 Å, and planarity was maintained about the C−N bond. The cyano group was kept linear, with a C3−C distance of 1.31 Å and a C−N triple bond distance of 1.16 Å. For (aminomethyl)borane, geometries were kept identical to those for trimethylene; the atomic numbers of the 1 and 3 carbons were changed to 7 and 5, respectively. The only degrees of freedom studied in either case were the torsions around the 1−2 and 2−3 bonds.

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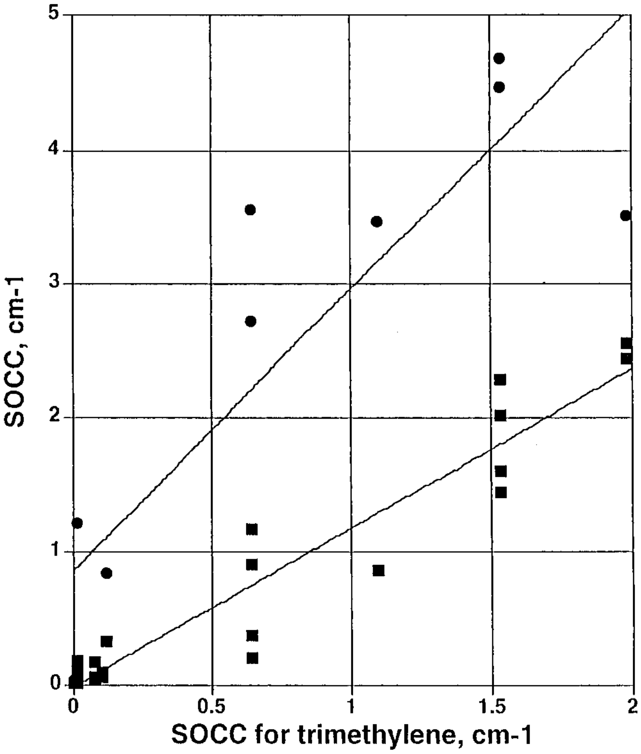

Figure 5. Spin−orbit coupling constants (SOCC) for H_2BCH_2-NH_2 (●) and 1-amino-3-cyano-1,3-propanediyl (■) plotted against SOCC for trimethylene at the same geometry. Trend lines: $y = 2.10x + 0.85$ ($H_2BCH_2NH_2$) and $1.19x - 0.015$ (1-amino-3-cyano-1,3-propanediyl).

Values for trimethylene agreed in essence with those previously reported for slightly different bond lengths and angles.[27] Figure 5 shows the plot of SOCC for 1-amino-3-cyanotrimethylene and (aminomethyl)borane against that for trimethylene at identical torsional angles (geometry details and a tabulation of the results are available as Supporting Information). Up to four geometries for 1-amino-3-cyanotrimethylene and two for (aminomethyl)borane correspond to a single geometry of trimethylene due to the asymmetries introduced by the substituents.

We note that the basic trend in either case is rough proportionality of SOCC to that for the trimethylene analogue. While there are conformational issues embedded in Figure 5, there are no experimental results which make their further examination profitable. We take the Franck−Condon component of the Golden Rule equation as constant. If the isc is assumed to arise from all conformations indiscriminately, the square of the slope of either plot then affords the predicted ratio of isc rate to that of trimethylene.[58] The ratios are 1.41 for 1-amino-3-cyanotrimethylene and 2.1 for (aminomethyl)borane. If we assume that isc arises only at the conformation affording the SOCC maximum, the ratios are ca. 1.5 and 5.0, respectively. As crude as the assumptions we make are, the difference between them is insignificant. Presumably substituent effects on isc rates would follow HMO spin density on the carbon bearing the substituent. Since the spin density is 1 at a simple alkyl radical terminus but only 1/7 at a para position of a benzyl radical, we predict ca. $1.5^{(1/7)} = 1.06$ for the acceleration of 1-(*p*-aminophenyl)-3-(*p*-cyanophenyl)-1,3-propanediyl relative to 1,3-diphenyl-1,3-propanediyl. This is about the precision of our measurements in the present series. The much larger values of SOCC and thus slope were expected for (aminomethyl)borane. By themselves they would predict much shorter lifetimes for analogous triplet biradicals, but we find large (ca. 30−40 kcal/mol) T_1-S_0 gaps which would tend to increase lifetime[1,3,45,54,59,60] and thus counteract the effect.

The cases we examined were intended to probe when polar substituents can accentuate the "hole−pair" terms enough to cause observable effects on isc rates. We conclude that such will occur only in extreme cases and that in an ordinary Hammett substituent series the effect will not be manifested. A substituent series for Norrish II biradicals, which are 1,4-butanediyl derivatives, similarly showed negligible polar substituent effects.[45] In light of the present calculations, we believe that observation was to be expected. A surprisingly long lifetime assigned to a Norrish II biradical analogue, the triplet species derived from β-dimethylaminopropiophenone,[60] for which the contribution of the hole−pair state to the singlet must be substantial, deserves reexamination. It is, however, possible that the long lifetime is caused by a large T_1-S_0 gap as pointed out above.

Is the lifetime of ca. 14 ns reasonable for the 1,3-diaryl-1,3-trimethylene biradical here described? Indeed so. SOC values of ca. 1 cm^{-1} are attainable at several low energy geometries (Figure 5 and supplementary table). By contrast, 1,4-diaryl-1,4-tetramethylene shows SOC values typically below 0.1 cm^{-1} for low energy geometries.[61] Since 1,4-diaryl-1,4-tetramethylenes show triplet lifetimes in the 200 ns range[3], the value for trimethylenes would be expected to be much shorter than 200 ns. The variation of SOC with conformation of these highly flexible biradicals prevents any more quantitative comparison without further studies. Recent reports have reached similar conclusions both theoretically and experimentally. Kita et al. studied 1,3-diaryl-1,3-cyclopentanediyl biradicals which avoid the conformational flexibility inherent in the present work.[43] Michl has developed a more rigorous version of the Salem−Rowland rules which highlights inter alia the present point and the crucial role of through bond coupling of SOC.[62] Bockmann and co-workers have developed a formatism for calculating SOC effects in organic molecules based on the Rumer spin eigenfunction and the second quantization.[63] Zimmerman has also studied SOC in α,ω-alkanediyls.[64]

Experimental Section

General. General experimental information was described in a previous paper.[65]

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[58] The singlet−triplet gap is expected to affect the isc rate. Unfortunately the calculations we performed are not able to give reliable estimates for S−T gaps. However, we note that there is little difference between the S−T gaps calculated for trimethylene and 1-amino-3-cyanotrimethylene at any geometry. Our calculations thus provide no evidence that differences in the S−T gap with substituent contribute to substituent effects on isc for substituted trimethylenes.

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Synthesis of 1,2-Diarylcyclopropanes Bearing Acetylphenyl Groups. The introduction of an acetyl group to the phenyl ring was carried out by two methods: (1) through a Friedel−Crafts acylation (method A) and (2) by methylation of a cyano group through the use of a Grignard reagent (method B).

Synthesis of *trans*- and *cis*-1,2-Bis(4-acetylphenyl)cyclopropanes (1a and 2a). General Procedure for Method A. Small portions of $AlCl_3$ were added to a mixture containing acetyl chloride and 1,2-diphenylcyclopropanes[66] in CS_2 within 30 min at room temperature. After 2 h of stirring, the reaction mixture was poured into a concentrated HCl/ice mixture and extracted with benzene:ether (1:1). The organic layer was then dried over Na_2SO_4. The solvent was evaporated and the residue chromatographed on silica gel. The unreacted 1,2-diphenylcyclopropanes were recovered from the hexanes eluent. From the hexane:benzene (1:1) eluent, 10−20% of 1-(4-acetylphenyl)-2-phenylcyclopropanes (**1b** and **2b**) were obtained, and from the benzene:ethyl acetate (98:2) eluent, 30−60% of **1a** was obtained. Repeated recrystallization of **1a** from acetone−methanol yielded pure **1a**: mp 171−172 °C; ^1H NMR ($CDCl_3$) δ 1.65 (dd, 2H, $J = 6$ and 9 Hz), 2.30 (dd, 2H), 2.52 (s, 6H), 7.50 (ABq, 8H, $\Delta\nu = 42$ Hz, $J = 9$ Hz); ^{13}C NMR ($CDCl_3$) δ 197.59, 147.70, 135.13, 128.70, 125.73, 29.05, 19.50; IR (KBr) 1646, 1578, 1330, 1248, 1170 cm^{-1}; MS (70 eV) m/z 278 (M^+). Anal. Calcd for $C_{19}H_{18}O_2$: C, 81.98; H, 6.52. Found: C, 82.02; H, 6.58.

2a was obtained by the photoreaction of **1a** (see text). Repeated recrystallization of the reaction mixture from hexane gave pure **2a**: mp 108.8−109.8 °C; ^1H NMR ($CDCl_3$) δ 1.52 (dd, 2H, $J = 6$ and 9 Hz), 2.46 (s, 6H), 2.55 (dd, 2H), 7.36 (ABq, 8H, $\Delta\nu = 42$ Hz, $J = 9$ Hz); ^{13}C NMR ($CDCl_3$) δ 197.77, 143.75, 134.93, 128.94, 127.97, 26.48, 25.11, 11.97; IR (KBr) 1650, 1590, 1346, 1260, 1172, 832 cm^{-1}; MS (70 eV) m/z 278 (M^+). Anal. Calcd for $C_{19}H_{18}O_2$: C, 81.98; H, 6.52. Found: C, 81.90; H, 6.43.

trans-1-(4-Acetylphenyl)-2-phenylcyclopropane (**1b**) was obtained by recrystallization of a mixture of **1b** and **2b** from hexane. **1b**: mp 50.3−51.1 °C; ^1H NMR ($CDCl_3$) δ 1.43 (dd, 2H, $J = 6$ and 9 Hz), 2.13 (dd, 2H), 2.45 (s, 3H), 7.08 (s, 5H), 7.42 (ABq, 4H, $\Delta\nu = 42$ Hz, $J = 9$ Hz); ^{13}C NMR ($CDCl_3$) δ 197.63, 148.58, 141.74, 134.85, 128.62, 126.07, 125.79, 125.63, 29.05, 28.17, 26.54, 18.92; IR (KBr) 1650, 1580, 1340, 1260, 1175, 800, 735, 680 cm^{-1}; MS (70 eV) m/z 236 (M^+). Anal. Calcd for $C_{17}H_{16}O$: C, 86.40; H, 6.83. Found: C, 86.30; H, 6.55.

cis-1-(4-Acetylphenyl)-2-phenylcyclopropane (**2b**) was isolated by through preparative HPLC. **2b**: oil; ^1H NMR ($CDCl_3$) δ 1.42 (dd, 2H, $J = 6$ and 9 Hz), 2.40 (dd, 2H), 2.42 (s, 3H), 6.98 (s, 5H), 7.36 (ABq, 4H, $\Delta\nu = 42$ Hz, $J = 9$ Hz); MS (70 eV) m/z 236 (M^+).

Synthesis of *trans*-1-(2-Acetylphenyl)-2-phenylcyclopropane (1c). General Procedure for Method B. 1-(2-Bromophenyl)-2-phenylcyclopropane was synthesized from 2-bromobenzaldehyde and acetophenone following a similar method as described in the literature.[66] **1c**: ^1H NMR ($CDCl_3$) δ 1.30−1.35 (m, 2H), 2.40−2.60 (m, 2H), 6.67−7.90 (m, 9H); MS (70 eV) m/z 274, 272 (M^+). This compound (9.7 mmol) was refluxed with CuCN (15.1 mmol) in *N*-methyl-2-pyrrolidone (20 mL) for 3 h. The reaction mixture was then extracted with benzene−ether and washed with water, and the organic layer was dried over Na_2SO_4. After removal of the solvent, the residue was chromatographed on silica gel. From hexane eluent, 1-(2-cyanophenyl)-2-phenylcyclopropane was obtained in a 94% yield: ^1H NMR ($CDCl_3$) δ 1.40−1.60 (m, 2H), 2.25−2.65 (m, 2H), 6.70−7.60 (m, 9H); MS (70 eV) m/z 221 (M^+). To a solution of CH_3MgI (10 mmol) in ether (20 mL) was added 1-(2-cyanophenyl)-2-phenyl-cyclopropane (2.7 mmol) in ether (10 mL) at room temperature. Dry benzene (10 mL) was added to the reaction mixture which was refluxed for 5 h and then stirred for 12 h. Acetic acid was added, and the mixture was heated to reflux for 4 h. The organic layer was washed with water and dried over Na_2SO_4. After the removal of the solvent, the residue was distilled under reduced pressure using a glass tube oven (9.3 Pa; 120 °C). 1-(2-Acetylphenyl)-2-phenylcyclopropane was obtained as a mixture of trans and cis isomers (**1c** and **2c**) in 67% yield. Pure **1c** and **2c** were obtained by careful distillation of the mixture. **1c**: oil; ^1H NMR ($CDCl_3$) δ 1.27 (dd, 2H, $J = 6$ and 9 Hz), 1.83−2.83 (m, 2H), 2.36 (s, 3H), 6.73−7.53 (m, 4H), 7.07 (s, 5H); MS (70 eV) m/z 236 (M^+). Anal. Calcd for $C_{17}H_{16}O$: C, 86.40; H, 6.83. Found: C, 86.20; H, 6.48. **2c**: oil; ^1H NMR ($CDCl_3$) δ 1.26 (dd, 2H, $J = 6$ and 9H), 1.88 (s, 3H), 2.53−2.94 (m, 2H), 6.40−7.53 (m, 9H); MS (70 eV) m/z 236 (M^+).

Other cyclopropanes were prepared by similar methods.

Photoisomerization of 1a and 2a. General Procedure. A benzene solution of **1a** (0.01 mol L^{-1}, 8 mL) was degassed by repeated freeze−pump−thaw cycles (four times) and then sealed in a Pyrex tube (Φ 10 mm). The sample was irradiated at 313 nm after which the reaction mixture was analyzed by HPLC (Daiseru Nucleosil Φ 4.6 mm × 150 mm, MeOH−water (7:3)). ^1H NMR analysis revealed the formation of **2a**, **3a**, and **4a**. **2a** was irradiated in a similar manner. Quantum yields were measured by the method of Parker.[68] The quantum yields obtained from argon-saturated solutions agreed with those obtained from degassed solutions.

Sensitized Photoreaction of 1a. Benzene solutions of **1a** (0.01 mol L^{-1}) containing triplet sensitizers such as acetophenone, benzophenone, and benzil were irradiated at the same time using a merry-go-round apparatus. The concentration of the sensitizer, determined by its extinction coefficient at 313 nm, was selected to absorb 90% of the light (OD = 20, $\epsilon_{\mathbf{1a}}$(313 nm) = 100). The quantum yields for benzophenone or benzil sensitized reactions were determined by the yields of **2a** relative to the sample containing acetophenone ($\Phi = 0.40$). The results are given in Table 3.

Preparative Photoreaction of 1a. A benzene solution (50 mL) of **1a** (1.7 mmol) was irradiated under an argon atmosphere for 5 h, after which the solvent was evaporated. **1a** was removed by recrystallization of the residue from hexane. Repeated recrystallization of the mother liquor from hexane yielded pure **2a**. A similar irradiation of **1a** (0.4 mmol) in benzene was carried out under an argon atmosphere for 54 h. **1a** and **2a** were removed by recrystallization from hexane. The mother liquor was evaporated and the residue dissolved in dimethoxyethane (0.5 mL). A mixture of **3a** and **4a** (2:1) was obtained by preparative HPLC separation in 42% yield. (*E*)-1,3-Bis(4-acetylphenyl)propene (**3a**): ^1H NMR ($CDCl_3$) δ 2.60 (s, 6H), 3.73 (d, 2H, $J = 7.3$ Hz), 5.96 (dt, 1H, $J = 7.3$ and 11.3 Hz), 6.67 (d, 1H, $J = 11.3$ Hz), 7.28−7.95 (m, 8H); MS (70 eV) m/z 278 (M^+). (*Z*)-1,3-Bis(4-acetylphenyl)propene (**4a**): ^1H NMR ($CDCl_3$) δ 2.60 (s, 6H), 3.64 (d, 2H, $J = 4.9$ Hz), 6.49 (m, 2H), 7.28−7.95 (m, 8H); MS (70 eV) m/z 278 (M^+).

Photoreaction of 3a and 4a. A benzene solution of a mixture of **3a** and **4a** (**3a**/**4a** = 2/1) (0.015 mol L^{-1}, 4 mL) was irradiated in a Pyrex tube for 4 days under an argon atmosphere. The reaction mixture was analyzed by GC, HPLC, and ^1H NMR. A mixture of **3a** and **4a** was quantitatively recovered.

Photoreaction of 1a in the Presence of Oxygen. A benzene solution of **1a** (0.015 mol L^{-1}, 4 mL) was irradiated in a Pyrex tube at 313 nm with vigorous oxygen bubbling. After the consumption of **1a** and **2a** within 1 h, the reaction mixture was analyzed by ^1H NMR and GC-MS. From the ^1H NMR spectrum, the formation of 3,5-bis(4-acetylphenyl)-1,2-dioxolane (**5a**), 4-acetylbenzaldehyde (**6a**), and 1,4-diacetylbenzene (**7a**) was confirmed. **5a** was formed as a mixture of cis and trans isomers (cis/trans = 7/3). The structure of **5a** was determined by the typical chemical shifts of 1,2-dioxolanes and their coupling pattern in the ^1H NMR spectrum in comparison with those of 3,5-diaryl-1,2-dioxolanes, which we have reported previously.[35] The formation of **6a** and **7a** was also confirmed by GC-MS. 3,5-Bis(4-acetylphenyl)-1,2-dioxolane (**5a**): ^1H NMR ($CDCl_3$) (trans) δ 3.13 (t, 2H, $J = 6.5$ Hz), 5.48 (t, 2H);

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(cis) 3.60 (dt, 1H, $J = 7.6$ and 12.2 Hz), 5.50 (t, 2H); other peaks were not assigned due to overlapping signals. 4-Acetylbenzaldehyde (**6a**): ^{1}H NMR ($CDCl_3$) δ 2.62 (s, 3H), 7.96 (s, 4H), 10.10 (s, 1H); MS (20 eV) m/z 148 (M^+). **1,4-Diacetylbenzene (7a).** To a solution of CH_3MgI (40 mmol) in dry ether (20 mL) was added 1,4-dicyanobenzene (10 mmol) in dry benzene (50 mL), and the mixture was then refluxed for 4 h. The solution was hydrolyzed with 50% AcOH and refluxed for 4 h. The organic layer was dried over Na_2SO_4 and the solvent evaporated to give 1,4-diacetylbenzene: ^{1}H NMR ($CDCl_3$) δ 2.64 (s, 6H), 7.99 (s, 4H); MS (20 eV) m/z 162 (M^+).

Laser Flash Photolysis. The laser flash photolysis experiments were carried out by well-known procedures.[3,67] The transients from compounds **1a**−**b**, **1e**−**k**, **2a**, and **3a**/**4a** were monitored at 310 or 315 nm. The concentration of the compound was $(1-4) \times 10^{-4}$ mol L^{-1}. These experiments were performed under nitrogen atmosphere.

Thermal Isomerization of 2a. A diethylene glycol solution of **2a** (1.29×10^{-3} mol L^{-1}, 0.3 mL) was placed in a Φ 5 mm NMR tube and saturated with argon. The sample was then heated to 174 °C (±1 °C) in an oil bath. The reaction mixture was analyzed by HPLC, and the yield of **1a** was determined. The logarithm of the concentration of **2a**, log[**2a**], vs reaction time was plotted. The rate constant for the thermal isomerization of **2a** to **1a** was estimated from the slope of the plot in the initial stage of the reaction, where the reverse reaction of **1a** to **2a** can be neglected. Rate constants at various temperatures (4 points) were obtained in the same manner. These rate constants were plotted as log k vs reciprocal of absolute temperature, T^{-1}, to generate an Arrhenius plot. From the slope and intercept of the plot, the activation energy, E_a, and the preexponential factor, A, were obtained.

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Supporting Information Available: Tables showing SOC values between S and T states of the three biradicals studied, with structure and geometry variations included. Spectral properties for **1d**−**k** (8 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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