Characterization of the Excited-State Reactivity of a Persistent Aryl-Substituted Allyl Free Radical

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A family of stable aryl-substituted allyl radicals 1 (9*H*-fluoren-9-yl-9-[9*H*-fluoren]-9-ylidenephenylmethyls) has been characterized by electronic absorption spectroscopy, semiempirical (AM1) molecular orbital calculations, and cyclic voltammetry. Photolysis of **1a** in aerated solvents that are poorer hydrogen atom sources than toluene resulted in oxygenation ($\phi_{OX} \sim 5 \times 10^{-4}$) and cleavage products. A thermally reversible photocyclization mechanism is proposed to explain the oxygenation of **1a** in inert solvents. Enhanced excited-state reactivity toward hydrogen and halogen atom donors was observed during the steady-state photolysis of **1a**. Electron transfer from naphthalene to an excited state of **1a** produces an extremely short lived (<30 ps) **1a** anion/ naphthalene radical cation geminate pair.

Introduction

The photolysis and photochemistry of radicals are topics of current interest.¹⁻¹⁹ Although considerable data concerning the ground-state reactivities of radicals are available, relatively few detailed studies of their excited-state properties have been reported.

The propensity of most radicals to facile ground-state reactions makes the observation of competing excited-state processes difficult. Ground-state instability can be circumvented by the use of two-photon laser techniques,^{5,11} with which the diphenylketyl^{4,6-8} and the diphenylmethyl radicals have been most extensively studied.^{1,2,10-17} The partitioning among several deactivation modes of excited diphenylmethyl radicals depends strongly on structure, especially on steric crowding near the radical center.¹¹ In general, benzylic radicals show higher reactivity in the excited state than in the ground state toward H-atom donors,^{1,13} halogen atom donors,^{1,2,17} and molecular oxygen.^{1,14} Fluorescence quenching of several diphenylmethyl radicals by electron transfer has also been reported.^{9,16,18,19}

Despite its photophysical utility, the two-photon generationexcitation technique poses some experimental difficulties (e.g., obtaining sufficient quantities for product analysis) that can be avoided by the study of radicals that are stable in the ground state. For example, we have previously shown that fluorescence, internal conversion, and ring cyclization are principal modes of relaxation in the photoexcited perchlorotriphenylmethyl radical.¹⁸ The perchlorodiphenylmethyl radical, in contrast, does not ringclose but instead fragments in the excited state.¹⁹ These perchlorinated excited radicals, like their hydrocarbon counterparts, exhibit higher rates of hydrogen and halogen atom abstraction than in the corresponding ground states. Efficient photoinduced electron transfer from the lowest lying excited states of perchlorotriphenylmethyl and perchlorodiphenylmethyl radicals with both electron donors and electron acceptors were also observed.

All stable radicals whose photoreactions have been investigated thus far are aryl-substituted perchlorinated methyl radicals. Although our understanding of the excited-state reactivity of such perchlorinated methyl radicals is not yet complete, we wished to extend our study to excited nonhalogenated allyl radicals. From the several tetraarylallyl radicals known to be thermally stable,²⁰ we have chosen derivatives 1 for detailed investigation. The photosensitivity of 1a has been reported, but neither the course nor the efficiency of its photoreactivity has been established by product or mechanistic studies.²¹



 Ia:
 R = H

 Ib:
 OMe

 Ic:
 CN

 Id:
 NO2

Our interest lies in establishing and understanding the relationship between the structures and reactivities of radicals **1a-d**, a series of stable, nonhalogenated free radicals. We are particularly interested in their potential use as visible light-activated redox initiators in view of their intermediate oxidation level between closed-shell anions and cations. Stable free radicals are ground-state doublets (with an open-shell electronic configuration), and upon photoexcitation excited doublet states are produced directly. How structural perturbations influence excited-state relaxation modes of excited doublets is a challenging question. In this paper, we describe the reactivity of the excited states of 1 (relative to their ground state) toward molecular oxygen, hydrogen and halogen atom donors, and naphthalene, a potential electron donor.

Results and Discussion

Characterization of the Ground State of 1a. Koelsch first prepared $1a^{22}$ and showed that it can be stored for decades in the solid state without noticeable decomposition. The inert nature of 1a and other nonhalogenated persistent radicals (such as triphenylmethyl, galvinoxyl, and TEMPO) has been primarily attributed to a rendering of the site bearing the largest fraction of radical character sterically inaccessible to radical traps, including molecular oxygen.²³

The ground-state conformation of 1a has been inferred from ESR studies of a closely related radical 2 and from molecular





Figure 1. Optimized geometry for 1a obtained by AM-1 semiempirical calculations. Bond lengths and angles are listed in Table I.

 TABLE I:
 Calculated Bond Distances, Angles, and Dihedral Angles for AMPAC Geometrically Optimized 1a

Bond Distances (Å)						
$C_1 - C_2$	1.419	C8-C9	1	1.404		
C ₂ -C ₃	1.418	C9-C10]	1.460		
$C_3 - C_4$	1.468	$C_{2}-C_{16}$	1	1.502		
C4-C5	1.415	$C_{16} - C_{17}$		1.418		
Cs-C6	1.404	$C_{17} - C_{18}$		1.405		
C6-C7	1.406	C ₁₈ -C ₁₉		1.405		
C7-C8	1.404					
	Bond Angles	(deg)				
	$C_1 - C_2 - C_3$		124.2			
	$C_1 - C_2 - C_{16}$		118.0			
	C ₂ -C ₃ -C ₄		126.0			
Dihedral Angles (deg)						
	C1-C2-C3-C4		40.0			
	$C_1 - C_2 - C_{16} - C_{17}$		59.1			

 TABLE II:
 Absorption Maxima of Stable Allyl Radicals

 1a-d in CH₂Cl₂
 1a

	wavelength (nm) (ϵ (cm ⁻¹ M ⁻¹))		
radical	$D_0 \rightarrow D_3$	$D_0 \rightarrow D_2$	$D_0 \rightarrow D_1$
1a	380 (4 200)	485 (29 400)	859 (1 580)
1b	435 (11 900)	503 (25 000)	890 (1 200)
1c	370 (31 00)	490 (23 700)	845 (1 080)
1d	430 (10 500)	515 (27 800)	870 (1 420)

orbital calculations. The π orbitals of the central allyl unit of tetraarylallyl radicals such as 1 and 2 cannot lie coplanar because of the steric demands of the fluorenyl groups bound at each end. Anomalous hyperfine splitting patterns reported in the ESR spectra of 2 have been explained as deriving from a twisted allyl framework,²⁴ the dihedral angle $C_1-C_2-C_3-C_4$ having been estimated as 37°. The minimum energy conformation of 1a resulting from AM-1 semiempirical calculations is shown in Figure 1, and selected calculated structural information is listed in Table I. These calculations estimate a $C_1-C_2-C_3-C_4$ dihedral angle of 40° for 1a, confirming the twisted nature of the allyl system, which is in accord with the dihedral angle measured for 2. Unfavorable steric interaction between the fluorenyl moieties in 1a is further demonstrated by the distorted $C_1-C_2-C_3$ bond angle, between the fluorenyl groups which is calculated to be 6.2° larger than the $C_1-C_2-C_{16}$ bond angle between the phenyl and the fluorenyl groups.

Absorption wavelength maxima and molar extinction coefficients for p-phenyl substituted tetraarylallyl radicals **1a-d** in methylene chloride are given in Table II. Both methoxy (**1b**) and nitro (**1d**) substitutions result in bathochromic shifts of the $D_0 \rightarrow D_1$, $D_0 \rightarrow D_2$, and $D_0 \rightarrow D_3$ transitions. In contrast, cyano substitution produces hypsochromic shifts of the $D_0 \rightarrow D_1$, and $D_0 \rightarrow D_3$ transitions, and a bathochromic shift for the $D_0 \rightarrow D_2$ transition in **1c**. The magnitudes of the absorption shifts in **1c** are lower than those in **1d** since a cyano group is a weaker acceptor

 TABLE III:
 Reversible Electrochemical Reduction and

 Oxidation Potentials of Stable Allyl Radicals 1a-d^a

	E _{1/2} (V vs SCE)		
radical	BDPA*/BDPA*	BDPA*/BDPA-	
1a	+0.67	-0.59	
1b	+0.63	-0.67	
1c	+0.73	-0.57	
1 d	+0.74	-0.44	

^a Mean value between the oxidative and reductive peak potentials obtained by cyclic voltammetry on a Pt electrode at room temperature in dry CH₂Cl₂ containing 0.1 M tetrabutylammonium perchlorate; scan rate 100 mV/s; \pm 30 mV.

than a nitro moiety. It is surprising that 1c exhibits hypsochromic shifts for the $D_0 \rightarrow D_1$ and $D_0 \rightarrow D_3$ transitions relative to 1a. The origin of this effect is not clearly understood, but cyano substitution on the benzyl radical also produces hypsochromic shifts.13 This effect has been explained as arising from an inversion of the energies of the two lowest lying excited states. Overall, the 5-30-nm absorption shifts for 1b-d (relative to 1a) are comparable to shifts observed upon substitution of diphenylmethyl^{14,16} and diphenylketyl radicals.^{6,8} Semiempirical molecular orbital calculations (AM1) produce a minimized energy for la when the C_2 -phenyl is rotated 59.1° from the plane of the central allyl core (dihedral angle of C_1 - C_2 - C_{16} - C_{17}). Even though this angle is relatively large, there is enough orbital overlap between the π system of the allyl core and the π system of the phenyl group to perturb the absorption spectrum. Slight shifting of the allyl nonbonding molecular orbital energy is expected, since twisting of the allyl skeleton gives rise to minimal spin density at C_2 ²⁴ In contrast, the energies of the allyl π bonding and antibonding orbitals will be drastically altered, since considerable spin density is found at C_2 . The absorption spectra are ultimately changed because the lowest energy electronic transitions involve the shifted π (or π^*) and minimally shifted (nonbonding) allyl molecular orbitals.

The cyclic voltammetric redox potentials of 1a-d in methylene chloride are shown in Table III. Radicals 1a-d displayed reversible one electron reduction and oxidation waves. The oxidation potentials in this series become more positive (1b < 1a < 1c < 1d) as the electron-donating capacity of the p-substituent increases. The oxidation potentials follow a linear Hammett relationship with σ^+ , yielding a ρ value of -0.32 ($R^2 = 0.92$). Substituent effects on the oxidation potentials of 1 are considerably smaller than for benzyl and cumyl radicals, where $\rho = -9.3$ and -6.8, respectively.²⁵ As compared with these benzyl radicals, the decreased sensitivity of the observed oxidation potential to the substituent in 1a-d can be rationalized by a significantly reduced orbital overlap of the perturbed phenyl group with the allyl core because of twisting caused by steric interaction. Maximum stabilization by the substituent can be achieved only in benzyl radicals in which the ring carbons can lie coplanar with the radical center. Moreover, redox potential shifts due to substituent effects are minor in 1 because of the low spin density at C_2 , as discussed above.

The reduction potentials of 1 become less negative (1b > 1a > 1c > 1d) as the electron-accepting ability of the p-substituent is enhanced. The reduction potentials show a reasonably linear dependence on σ , yielding a slope of 0.55, but with a low correlation coefficient ($R^2 = 0.77$). The approximately 10-fold decrease in sensitivity to the substituent of the reduction potentials for 1a-d than with benzyl or cumyl radicals²⁵ presumably arises because of diminished orbital overlap between the aryl group and the allyl π -system, and the low spin density at C2.²⁴

Photooxygenation of 1a in Poor Hydrogen Atom Solvents. In the dark, **1a** is stable in the solvents listed in Table IV for several weeks, irrespective of whether the solution is aerated or degassed. Irradiation for up to 72 h of a rigourously degassed solution of **1a** $(5 \times 10^{-3} \text{ M})$ with either UV or visible light produced no observable chemistry in any of these solvents. However, photolysis

TABLE IV: Quantum Yields for the Unimolecular Photoinduced Oxygenation of 1a in Various Solvents

	$\phi_{\rm ox} imes 10^4 a$		
solvent	air saturated	O ₂ saturated	BDE ^b (kcal/mol)
C ₆ H ₆	6 ± 1	5±1	110.9 ± 2
CH ₂ Cl ₂	7 ± 1	6 ± 1	100.6 🛳 1
CH ₃ CO ₂ C ₂ H ₅	9 ± 2	11 ± 2	98.3 ± 2
CHCl ₃	17 ± 3	14 ± 3	95.8 🖴 1
C ₆ H ₁₂	9 ± 2	12 ± 2	95.5 1
CH ₃ OH	10 ± 2	9 ± 2	94.0 ± 2
CH ₃ CN	8 ± 2	10 ± 2	93.0 ± 2

^a Sum of quantum yields for products 3–5, irradiation wavelength 350 \pm 30 nm. ^b Bond dissociation energies for the weakest solvent C–H bond.⁴⁰

of the same solutions of 1a, when saturated with oxygen, gave complete reaction in less than 12 h.

The quantum yields for disappearance of 1a varied only slightly with solvent for solvents with C-H bond dissociation energies weaker than 100 kcal/mol, as would be expected if the solvent were participating in the decomposition of the excited radical. A probable reaction of excited stata 1a with the solvent would be atom abstraction, although no products attributable to this process could be isolated from aerated solution. Although the rates of decomposition of 1a in these solvents qualitatively follow the bond dissociation energies of the weakest bond in each solvent, the absence of reduced product indicates that this relatively small effect derives from differential solvation rather than hydrogen atom abstraction.

The nature of the photochemical reaction of 1a with molecular oxygen in CH_2Cl_2 (a poor hydrogen atom donating solvent) was probed by product analysis and kinetics. Upon steady-state photolysis of 1a in CH_2Cl_2 saturated with oxygen, products 3–5 are formed, eq 1.



The reported product yields, based upon the amount of consumed 1a at approximately 10% overall conversion, are isolated yields after chromatography. The identity of the products obtained are roughly independent of solvent: only 3-5 could be isolated in each of the solvents listed in Table IV. Quantum yields for photobleaching of a 5×10^{-5} M of solution of 1a in CH₂Cl₂ are invariant, within experimental error, with dissolved O₂ concentration, when a molar excess oxygen is present in either an air-saturated or O2-saturated solution, Table IV. The absence of an oxygen concentration effect on the quantum yield for photobleaching of 1a precludes bimolecular quenching by oxygen as a route to products. Therefore, a photoinduced unimolecular process must generate one or more long-lived intermediates which are slowly trapped by O_2 in a dark secondary process that leads to oxygenation. Photoinactivity in the absence of oxygen requires that subsequently the intermediate thermally revert to 1a. Analogous thermal reversion after oxygenation is also required to rationalize the products observed in the presence of O_2 . The formation of 3 can be ascribed to a chemical sequence in which

SCHEME I: Proposed Mechanism for the Oxygenation and Hydrogen Atom Abstraction Reaction of Excited 1a.



coupling of molecular oxygen with the metastable intermediate at what was originally the C_7 position (Figure 1) of **1a**, whereas product **4** arises from an analogous coupling at C_1 . Attempts to observe the expected peroxide intermediate by *in situ* IR spectroscopy were unsuccessful. The chemical yield of **4** was decreased to 14% by prolonged irradiation of the photolysis mixture to complete consumption of **1a**, as that of **5** increased to 17%, demonstrating that product **5** arises as a secondary photoproduct derived from **4**.

Although we were unable to directly observe the intermediate, we propose that a thermally reversible photocyclization of **1a** leads to the plausible intermediate **6**. Photocyclizations of this



type are well documented for cis-stilbene and related compounds,26 as well as for perchlorotriphenylmethyl radicals¹⁸ and α -substituted diphenylmethyl radicals.¹¹ Inspection of AM-1 geometrically optimized structures of 1a and 6 show that the radical center in the cyclized intermediate is sterically more accessible to an external reagent than is 1a itself (which had been earlier shown to be unreactive toward O_2). The stability of radical 1a derives from steric shielding by adjacent hydrogen atoms, and an average separation of about 2.4 Å from these hydrogen atoms to the radical center has been calculated by AM-1 molecular orbital calculations. Photocyclization of 1a by forming a bond between C_5 and C_{17} causes considerable distortion of the molecular framework, the distance from the radical center to hydrogens H8 and H_{13} being increased to approximately 2.8 Å (supplementary material) easing approach by molecular oxygen. Furthermore, resonance stabilization in 1a is disrupted by cyclization to 6.

A proposed mechanism that accounts for both the independence of the reaction rate on dissolved oxygen concentration and the product distributions observed in the photooxygenation of **1a** is shown in Scheme I. Intermediate **6**, formed by a photochemical cyclization, is trapped by oxygen in a slow dark secondary reaction that involves conversion of the peroxy radical to a monooxygenated species and thermal reversion (by aromatization) of the cyclized product, ultimately generating products 3–5. Several attempts to verify this photocyclization pathway by isolation of cyclized products or by detection of the cyclized intermediate with transient spectroscopy were unsuccessful, presumably because of the low quantum yield for the generation of 6. (A lower limit to the cyclization quantum yield is approximately 5×10^{-4} .)

Steady-State Photolysis in Hydrogen-Donating Solvents. As with the solvents in Table IV, a solution of 1a in toluene is stable in the dark for extended periods. The photolysis of 1a in toluene, however, led to several products, eq 2.



Compounds 3-5 are produced by the reaction of the photogenerated intermediate with molecular oxygen, as described above. Photoproduct 7 is generated by hydrogen abstraction by excited 1a from toluene. The formation of 8 is likely the result of trapping of the benzyl radical generated by hydrogen atom transfer in the formation of 7 with a ground state 1a, when the photolysis is conducted under deaerated conditions. When the photolysis is carried out in O₂-saturated solution, 8 cannot be isolated. Instead, oxygen intercepts the benzyl radical, ultimately generating benzaldehyde 9.

Kinetics of Hydrogen Atom Abstraction by Excited 1a. Steadystate irradiation of 1a in the presence of several hydrogen atom sources (toluene, diphenylmethane, and triphenylmethane) led to bleaching of the visible absorption bands of the radical. Two photoprocesses account for the disappearance of 1a: the intramolecular isomerization discussed above (which leads ultimately to oxygenation products) and a second route involving direct atom abstraction in the excited state, as shown in the isolation of 7 and 8. (In CH_2Cl_2 , the former route dominates.) No wavelength dependence of quantum yields for hydrogen atom transfer to excited 1a could be seen, unlike the photoreactions of perchlorotriphenylmethyl and perchlorodiphenylmethyl radicals which are wavelength-dependent.

The quantum yields for photoinduced disappearance of 1a in the presence of N_2 -purged hydrogen donating solvents are higher than those observed when the photolysis is conducted in oxygensaturated solution, Table V. With a N_2 purge, the steady-state concentration of dissolved oxygen is sufficiently low that the benzyl radical formed by initial hydrogen atom abstraction couples with ground state 1a, as suggested by the product studies discussed above. The kinetics suggest that a high yield of 8 should be obtained, but the low yield of 8 in N_2 -purged solutions presumably results from decomposition during isolation or destruction during photolysis by efficient secondary photochemistry. A competitive quenching of doublet excited 1a by oxygen and toluene can be excluded, since the quantum yield for hydrogen atom abstraction

TABLE V: Quantum Yields for the Photobleaching of 1a by Various Hydrogen Atom Donors in $CH_2Cl_2^a$

	$\phi_{bl} imes 10^{4} {}^{b}$			oxidation	
H-atom donor	N ₂ purge O ₂ purge		BDE ^c (kcal/mol)	potential ^d (V vs SCE)	
toluene	22 ± 4	10 ± 2	88.141	+2.40	
diphenylmethane triphenylmethane	300 ± 60 900 ± 180	90 ± 18 400 ± 80	81.4 ⁴² 80.8 ⁴³	+2.31 +2.18	

^a Concentration of hydrogen atom donor is 1.0 M, N₂-purged solution, irradiation wavelength 350 ± 30 nm. ^b Measured by disappearance of **1a** absorption at 485 nm. ^c Bond dissociation energy of the weakest C-H bond in the H-atom donor. ^d Irreversible oxidative peak potentials for hydrocarbons obtained by cyclic voltammetry on a Pt electrode at room temperature in dry CH₃CN containing 0.1 M tetrabutylammonium perchlorate; scan rate 100 mV/s; ± 30 mV.

 TABLE VI:
 Quantum Yields for Photobleaching of 1a in

 CH₂Cl₂ by Hydrogen Atom Abstraction from Several

 Substituted Toluenes^a

H atom donor	$\phi_{b1} imes 10^{4}$ b	σ+	oxidation potential ^d (V vs SCE)
p-tolunitrile	9 ± 2	+0.66	>+2.5
toluene	22 ± 4	0.00	+2.40
<i>p</i> -fluorotoluene	41 ± 8	-0.07	>+2.5
<i>p</i> -phenyltoluene	71 ± 14	-0.17	+1.90
p-methoxytoluene	120 ± 20	-0.78	+1.62

^a Concentration of substituted toluene donor is 1.0 M, N₂-purged solution, irradiation wavelength 350 ± 30 nm. ^b Measured by disappearance of **1a** absorption at 485 nm. ^c Irreversible oxidative peak potentials for hydrocarbons obtained by cyclic voltammetry on a Pt electrode at room temperature in dry CH₃CN containing 0.1 M tetrabutylammonium perchlorate; scan rate 100 mV/s; ± 30 mV.

decreases only 50%, accounted for above, with drastic increases in oxygen concentration.

The quantum yields for disappearance of 1a were strongly dependent upon the hydrogen atom donating ability of the quencher, Table V. A measure of the ease of hydrogen abstraction from a given hydrocarbon is its C-H bond dissociation energy, which are also listed in Table V. As the benzylic C-H bond dissociation energy decreases in the series, an increase in the quantum yield for disappearance of 1a is observed.

Hydrogen atom transfer could take place, in principle, though an initial electron transfer from the donor to excited 1a, followed by proton transfer within the resulting radical ion pair. If so, the abstraction rates should parallel the oxidation potential of the donor. Although this order holds for toluene, diphenylmethane and triphenylmethane, p-methoxytoluene, with a less positive oxidation potential (Table VI), exhibits a lower quantum yield for hydrogen atom abstraction than diphenylmethane or triphenylmethane. The lack of a correlation between the oxidation potentials and the quantum yields for hydrogen atom transfer from these donors to excited **1a** suggests that the photoreduction observed in arylmethanes and substituted toluenes probably involves simple atom transfer. The relative reactivity for hydrogen atom abstraction by excited 1a from toluene:diphenylmethane: triphenylmethane (1:14:41) differs than that observed for the ground state of the benzyl radical (1:21:92)²⁷ and for the Br radical (1:10:17).²⁸ The excited state of **1a** is thus more reactive (and less selective) than a ground state benzyl radical, approaching bromine in reactivity.

The quantum yields for disappearance of 1a in CH_2Cl_2 were also directly proportional to the concentration of the potential hydrogen atom source, as evidenced by linear Stern–Volmer plots for each member of the series. This is consistent with a mechanism in which bimolecular quenching of the excited state of 1a leads irreversibly to products. The Stern–Volmer rate constants for excited state quenching of 1a by toluene, diphenylmethane, and triphenylmethane are 0.0010, 0.012, and 0.050 M⁻¹, respectively.

The polarity and degree of bond breaking in the transition state for hydrogen atom abstraction from substituted toluenes by

TABLE VII: Quantum Yields for Photobleaching of Excited Stable Allyl Radicals 1a-d by Atom Abstraction (H from Triphenylmethane and Br from Carbon Tetrabromide)⁴

	$\phi_{b1} imes 10^{4 b}$	
radical	triphenylmethane	CBr ₄
1a	90 ± 18	850 ± 170
1b	100 ± 20	1500 ± 300
1c	150 ± 30	660 ± 130
1d	400 ± 80	900 ± 180

^a In CH₂Cl₂, concentration of atom donor is 1.0 M, N₂-purged, irradiation wavelength 350 ± 30 nm. ^b Measured by disappearance of 1a absorption at 485 nm.

excited 1a can be determined readily by a linear free energy relationship.²⁹ The quantum yields for hydrogen abstraction from several substituted toluenes by excited 1a are shown in Table VI. These data yield a linear Hammett plot ($\rho = -1.2$, correlation coefficient = 0.995). The negative slope indicates that partial positive charge develops at the benzylic carbon of the substituted toluene and that there is considerable bond breaking in the transition state. The magnitude of the ρ value is comparable to that observed for hydrogen abstraction from toluenes by a ground-state CCl₃ radical, where p = -1.4.³⁰

The polarity of the transition state for hydrogen atom abstraction by excited state radicals **1a**-d from triphenylmethane, as discussed above, was further reinforced by probing the effect of donor or acceptor substituents on the radical, Table VII. The quantum yield for bleaching of **1b** was not appreciably higher than that observed for **1a**, but cyano substitution in **1c** and nitro substitution of **1d** produced an enhanced quantum yield for hydrogen atom abstraction over that in **1a**, presumably by stabilizing the incipient negative charge on the radical in the transition state.

An upper limit for the excited-state lifetime of 1a can be obtained from the maximum observed quantum yield of bimolecular quenching and the calculated rate of diffusion control in methylene chloride at room temperature.³¹ From the maximum quantum yield of 0.04 for triphenylmethane at a 1.0 M quencher concentration, this analysis yields an upper limit of 4 ps for the excited-state lifetime of 1a. The excited state lifetime is expected to be shorter, since hydrogen atom abstraction by excited radicals from hydrogen atom donors is not diffusion controlled.¹ This estimated lifetime is consistent with the absence of observable transient excited states with lifetimes greater than 30 ps in methylene chloride solution upon flash excitation and with the observation that no steady state fluorescence from 1a could be observed in either any solvents at room temperature or in a 3-methylpentane glass at 77 K. The short lifetime could be a consequence of substantial vibronic coupling between the excited and ground state, resulting in efficient radiationless relaxation. The near-IR absorption (Table I) bands observed in these radicals are predictive of an efficient radiationless internal conversion caused by the small energy gap between the lowest excited and ground states.

Reaction with Halogen Atom Donors. Excited 1a was also reactive towards compounds with abstractable halogen atoms. Although CH₂Cl₂ is inert toward hydrogen or chlorine abstraction, CHCl₃, CCl₄, CHBr₃, CBr₄, and CH₃I are all reactive toward excited state 1a. Steady-state photolysis in CH₂Cl₂ containing these various halogen atom donors leads to a highly complex product mixture and product studies were not viable. Although there is no direct evidence for halogen abstraction, excited-state atom transfer is a reasonable pathway for decomposition of 1a. The kinetics of **1a** decomposition could be readily followed by monitoring the initial rate of photobleaching. The quantum yields of photobleaching of the 1a in the presence of several potential halogen atom donors are listed in Table VIII. The observed quantum yields qualitatively depend on the lability of the C-X bond as reflected by its bond dissociation energy. This correlation is suggestive of an atom abstraction reaction. The order of these

TABLE VIII: Quantum Yields for the Photobleaching of Excited 1a by Atom Abstraction from Various Halogen Atom Donors in CH₂Cl₂^a

halogen atom donor	$\phi \times 10^{4 b}$		BDE	reduction potential ^d
	N ₂ purge	O ₂ purge	(kcal/mol)	(V vs SCE)
CHCl ₃	<1	<1	79.0 ± 4.0^{44}	-1.9149
CCl4	11 ± 2	11 ± 2	70.0 ± 2.044	-1.4049 (-0.33)e,50
CH ₃ Br	<1	<1	70.3 ± 1.0^{45}	-1.7751
CHBr ₃	43 ± 9	44 ± 9	62.0 ± 1.8^{46}	(-0.26)*
CBr4	850 ± 170	800 ± 170	56.2 ± 1.8^{47}	(-0.08) ^{e,50}
CH₃Ì	15 ± 3	13 ± 3	56.3 ± 1.0^{48}	-1.37 ⁵¹

^a Concentration of halogen atom donor is 1.0 M, irradiation wavelength 350 ± 30 nm. ^b Measured by disappearance of **1a** absorption at 485 nm. ^c Bond dissociation energies for the weakest C-X bond. ^d Measured in CH₃CN. ^e Measured in CH₃CN, vs mercury pool.

dissociation energies correlates reasonably well with the order of the quantum yields for the photoinduced disappearance of **1a**. The halogen atom donors exhibited linear Stern–Volmer plots for CBr₄, CHBr₃, CCl₄, and CHCl₃, yielding reaction rate constants of 0.78, 0.043, 0.011, and <0.0002 M⁻¹, respectively, demonstrating bimolecular quenching of excited **1a**. Unlike the reactivity patterns observed with hydrogen atom donors (Table V), the quantum yields for photobleaching by these halogen atom donors were insensitive to O₂, Table VIII.

The efficiency of decomposition of excited 1a in CBr₄ is 80 times greater than in CCl₄. This ratio is comparable to the 100-fold difference for abstraction from these donors by ground state α -methylbenzyl radicals³² but less than the 1000-fold preference by manganese carbonyl radicals³³ or alkyl radicals.³⁴

In principle, the mechanism operative in the interaction with these halocarbons may involve initial electron transfer, since these quenchers all have high electron affinities. The quenching of the excited states of TEMPO and other nitroxyl radicals by CCl₄ by chlorine atom abstraction has been shown to take place by electron transfer.³⁵ Electron-transfer fluorescence quenching has also been shown to occur through interaction of the lowest doublet diphenylmethyl radical,9 and substituted diphenylmethyl radicals¹⁶ with CCl₄. Here, the halogen atom donor presumably can accept an electron from excited 1a to form the corresponding radical anion which undergoes rapid bond cleavage, resulting in the generation of a halide ion and a carbon-based radical. However, estimates of the excited-state oxidation potential of 1a from the ground state oxidation potential and the position of 0,0 band in its absorption spectrum is -0.7 V (vs SCE), a value clearly insufficient to reduce the halocarbon quenchers, thus rendering electron transfer thermodynamically infeasible. Interestingly, similar quantum yields for photobleaching of excited 1a are obtained in CCl₄ and CH₃I, where different halogens are being transferred, but whose reduction potentials differ by only 40 mV.

The transition state polarity for photobleaching of 1a from potential halogen donors was also probed by substituting electron ' donors and acceptors onto 1a. The quantum yield for photoinduced disappearance of radicals 1a-d in CH₂Cl₂ in the presence of 1.0 M CBr₄ are given in Table VII. The observed quantum yields of 1a, 1c, and 1d are approximately equal, within experimental error, but that of 1b is approximately doubled. The enhanced electron donating character of 1b compared with others in this series is caused by the methoxy group, which increases the rate of halogen atom abstraction by stabilizing a positive charge at the radical center in the transition state.

Reaction with Electron Donors. The possibility of electron transfer between excited **1a** and an aromatic donor (naphthalene) was probed by transient spectroscopy. **1a** in N₂-purged CH₂Cl₂ was excited by the 532-nm laser pulse from the second harmonic of a Nd:YAG laser in the presence of naphthalene (0.1 M). The appearance of a transient with an absorption band at 650 nm, closely resembling that of the anion of **1a**,³⁶ clearly establishes the electron-transfer character of this reaction. The relaxation

of this transient, presumably by recombination of this photogenerated geminate ion pair, is also extremely fast (<30 ps).

Conclusions

The electronic structure of **1a** is perturbed by substitution on the 4-position of the phenyl group, as evidenced by shifts in both the absorption maxima and the reversible redox potentials. AM-1 calculations of the minimum energy conformation reveal significant ground state twisting of **1a** (37°) in accord with ESR results in a closely related radical.

Photooxygenation of **1a** is observed in solvents which are poorer hydrogen atom sources than toluene. A thermally reversible photoinduced cyclization is proposed to explain the oxygenation of excited **1a**.

The lowest lying excited state of 1a is reactive towards hydrogenor halogen-atom donors and at least one electron donor (naphthalene), whereas the ground state exhibited no such reactivity. This behavior is similar to that of other excited radicals (such as diphenylmethyl and diphenylketyl) where enhanced reactivity relative to the ground state has been reported. The rates of hydrogen atom abstraction from 4-substituted toluenes vary linearly with σ^+ ($\rho = -1.2$), implying partial positive charge at the benzylic carbon and considerable bond breaking in the transition state. The transition state for hydrogen atom transfer from toluene to the excited state of 1a is comparable in polarity as hydrogen atom transfer to ground-state CCl₃ radicals. Hydrogen atom or halogen atom abstraction rates depend on quencher concentrations, as is consistent with abstraction through bimolecular quenching of an excited doublet state. The quantum yield of atom abstraction by excited 1a increases with decreasing bond dissociation energies of the C-X bond in a series of atom donors. Quantum yields for atom abstraction by 1a-d are also dependent on the nature of the p-substituent on the aryl ring.

The excited state of the parent radical 1a could not be observed directly because of its extremely short lifetime (<30 ps), presumably a consequence of efficient internal conversion to the ground state by virtue of a low energy gap between these states. This very short lifetime limits the utility of these stable radicals as efficient visible light sensitizers.

Experimental Section

Reagents. Fluorene, p-nitrobenzaldehyde, p-cyanobenzaldehyde, bromine (Aldrich), benzaldehyde, p-methoxybenzaldehyde (Merck), potassium ferricyanide, cyclohexane, ethanol (Midwestern Grain Products), tetrabutylammonium perchlorate (Southwestern Analytical), and naphthalene (Kodak) were used without further purification. All solvents were dried and distilled before use: dimethylformamide (Baker), chloroform (Baker), and triethylamine (Aldrich) were dried over molecular sieves; methylene chloride and acetonitrile (Mallinckrodt) were distilled from calcium hydride; tetrahydrofuran (Aldrich spectrograde), benzene (Baker), and toluene (Mallinckrodt) were distilled from metallic sodium; and methanol was distilled from potassium ethoxide. Carbon tetrachloride (Baker), diphenylmethane, tolunitrile, 4-chlorotoluene, 4-methylanisole, and anisole were purified by simple distillation. Triphenylmethane and carbon tetrabromide (Aldrich) were recrystallized twice from ethanol.

Electrochemical Measurements. A Bioanalytical Systems 100 potentiostat equipped with a Houston Instruments DMP-40 plotter was used for cyclic voltammetric (CV) measurements. A three-electrode configuration, consisting of a platinum button working electrode, a Ag/AgCl quasi-reference electrode, and a platinum auxiliary electrode, was used. Typically, CV measurements were made for 10⁻⁴ M solutions in methylene chloride or acetonitrile containing 0.1 M tetrabutylammonium perchlorate. Oxygen was removed by an argon purge. CV traces were recorded at room temperature under argon at a scan rate of 100 mV/s.

Molecular Orbital Calculations. The geometry of the radical 1a was optimized on a microVAX computer Model 3100, using version 2.1 of AMPAC, a semiempirical molecular orbital package described elsewhere.³⁷

Spectral Measurements. Fluorescence spectra were recorded on a SLM Aminco SPF-500 spectrofluorometer equipped with an IBM 6180 plotter. Absorption spectra were recorded on a Hewlett-Packard 8451-A diode array spectrophotometer equipped with a Hewlett-Packard 7470 plotter. Near-infrared (NIR) absorption spectra were recorded on a Perkin-Elmer Lambda 7 instrument equipped with a Perkin-Elmer 5200 data station. Electron spin resonance (ESR) spectra were recorded on an IBM Model 300 ESR spectrometer. Nuclear magnetic resonance (NMR) spectra were recorded in CDCl₃ on a Nicolet QE-300 spectrometer referenced to tetramethylsilane as internal standard. High-resolution electron impact mass spectra were obtained on VGZAB2-E mass spectrometer. Gas chromatography/mass spectrometry analyses were performed on a Varian 3400 GC automated with a Finnigan MAT 700 MS instrument using a 25-m DB-5 capillary column.

Steady-State Photolysis. A 50-mL aliquot of a 5×10^{-3} M stock solution of 1a in methylene chloride or toluene containing measured amounts of a desired quencher was purged with either a slow stream of O_2 or nitrogen for 1 h. The resulting solution was sealed into a Pyrex flask and was irradiated in a Rayonet RPR-100 merry-go-round photoreactor equipped with phosphorcoated low pressure mercury arcs blazed at 350 nm for periods of up to 12 h. Identical dark control reactions were prepared, except being covered by aluminum foil. The progress of the photolysis was monitored by following the bleaching of the BDPA absorbance at 485 nm. Quantum yields were determined against potassium ferrioxalate as an actinometer.38 After termination of the irradiation, the solvent was removed under reduced pressure, and the products were separated on a Harrison Research (Model 8924) chromatotron using CCl₄ as eluent. The photoproducts were characterized by ¹H and ¹³C NMR, IR, and low-resolution mass spectrometry. Irradiation of an O₂-saturated methylene chloride solution of 1a, at 10% conversion, monitored by bleaching of 1a at 485 nm gave, after chromatographic separation, 3 (3.5 mg, 32%), 4 (3.2 mg, 29%), and 5 (0.4 mg, 5%). Irradiation of 1a in N₂-purged toluene gave, at 10% conversion of 1a, after chromatographic separation, 3 (0.8 mg, 7%), 4 (0.2 mg, 2%), 5 (0.5 mg, 10%), 7 (2.2 mg, 21%), 8 (0.5 mg, 4%). For 8, three isomers were additionally separated and detected by GC/MS. Irradiation of 1a in O₂-saturated toluene gave, at 10% overall conversion of 1a, after chromatographic separation, 3 (4.5 mg, 41%), 4 (1.1 mg, 10%), 5 (1.6 mg, 32%), 7 (0.2 mg, 2%), 9 (0.2 mg, 8%). In the dark, 1a in each solvent showed no decomposition whatsoever for periods of weeks.

Transient Absorption Spectroscopy. Time-resolved flash photolysis experiments were conducted on a frequency-doubled modelocked Nd:YAG laser (Quantel YG402, approximately 30 mJ at 532 nm). Absorptive transients were monitored with a conventional high-pressure Xe lamp, monochromator, photomultiplier arrangement.³⁹ Digitized signals were passed to a PDP 11/70 computer for analysis.

Synthesis. The radicals 1a-d were prepared by the method described by Negebauer and Kuhn.³⁶ The appropriately p-substituted benzaldehyde 10a-d was condensed with fluorene upon treatment with sodium ethoxide in ethanol to yield the substituted 9-benzylidenefluorenes (11a-d). Subsequently, 11a-d were brominated with Br₂ in acetic acid to yield 12a-d. 12a-d were converted to 1a-d by treating with fluorene and sodium ethoxide in ethanol and subsequently oxidizing with potassium ferricyanide. Spectral characterization data and melting points of 1a-d, 11a-d, and 12a-d are submitted as supplementary material.

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Supplementary Material Available: Table listing all bond distances, bond angles, and dihedral angles for the AMPACcalculated optimized geometry of 1a and spectral characterization of radicals 1a-d, radical precursors 11a-d, 12a-d, and photoproducts (10 pages). Ordering information is given on any current masthead page.

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