CHEMISTRY
A EUROPEAN JOURNAL

DOI: 10.1002/chem.200600011

α-Carbonyl Substituent Effect on the Lifetimes of Triplet 1,4-Biradicals from Norrish-Type-II Reactions

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Abstract: Triplet 1,4-biradicals were generated by Norrish-Type-II hydrogen transfer from α-heteroatom-substituted β-branched butyrophenones **1–6** and detected by laser flash absorption measurements. For three oxy-substituted compounds **2–4** ($R_\alpha = OH$, OCOMe, OCOOEt) comparable lifetimes were determined in acetonitrile (roughly 1.5 μs). In benzene, divergent trends were observed: for the hydroxy compound **2** a lower lifetime of 790 ns was determined, whereas for **3** and **4** the lifetimes increased to 4.9 μs. Photolyses of the α-amino-substituted compounds **1** and **6** resulted in transient species with significant lower lifetimes (for **1** 160 ns in benzene and 450 ns in acetonitrile; for **6** <100 ns in both solvents). The mesyloxy substrate **5** undergoes rapid C–O bond cleavage upon photolysis and no transient triplet species were detected. Computational (UB3LYP/6–31G* and natural don orbital (NBO) analyses) results supported the assumption of a negative hyperconjugative interaction strongly stabilizing α-oxy-substituted over α-amino-substituted radicals.

Keywords: hyperconjugation • laser spectroscopy • photochemistry • radicals

Introduction

Triplet 1,4-biradicals (butane-1,4-diyls) have been investigated in detail because they constitute important reactive open-shell intermediates in thermal and photochemical reactions.[1–3] The classical photochemical process resulting in 1-hydroxybutane-1,4-diyls is the Norrish-Type-II reaction, a γ-hydrogen transfer initiated from an electronically excited carbonyl state.[4,5] Aryl-substituted ketones preferentially involve the first excited triplet state. Three competing pathways are known for the Norrish-Type-II reaction of aryl alkyl ketones from the triplet state (T_1) via the corresponding triplet 1,4-biradicals: Yang cyclization, β-cleavage, and hydrogen back transfer reconstituting the starting material.[6] The product selectivity ratios for Yang cyclization/β-cleavage have been studied for a series of ketones.[7–10] It has been confirmed that, among other factors, the intermediate hydrogen bonding and spin orbit coupling (SOC) geometries preferentially govern the relative product yields.[11]

To characterize the geometry and lifetimes of these 1,4-biradicals, laser-flash transient absorption spectroscopy is an important tool. It has been reported that the lifetime of 1-hydroxybutane-1,4-diyls generated by the Norrish-Type-II process is usually shorter than 200 ns.[3] Herein we report a remarkable effect of substituents at the α-position of β-branched butyrophenone derivatives upon the lifetime of triplet 1,4-biradicals. The lifetimes are found to vary by a factor of more than 200, from low (<25 ns) up to unusually high (5 μs) lifetimes. The structures of the α-substituted butyrophenones used in this study (**1–6**) are shown here. The photochemistry of these compounds has already been evaluated by us[7,8] and by Wessig et al.[12] for the mesylate **5**.

Results and Discussion

Transient absorption: The transient absorption experiments of **1–6** were performed by using a 308 nm XeCl excimer

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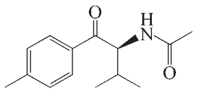

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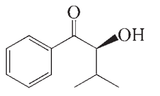

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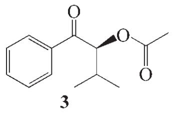

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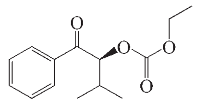

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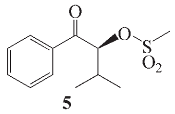

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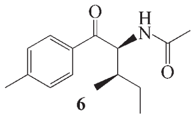

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laser (25 ns, 8 mJ pulse^{-1}) in argon-saturated acetonitrile (AN) and benzene (BZ) at room temperature. The transient absorption spectra and time profiles observed during the laser flash photolysis of **1** and **3** in BZ are shown in Figure 1. Those for the other compounds (**2**, **4**–**6**) and acetophenone as the triplet carbonyl model compound are given in the Supporting Information. The transient absorption band was observed around 350 nm for **1** and 440 nm for **2**–**4** during the 308 nm excitation. The transient absorption spectra of **1**–**4** are clearly not due to the triplet states, which should have similar absorption spectra to that of acetophenone in the T_1 state with a characteristic absorption at 330 nm.[13]

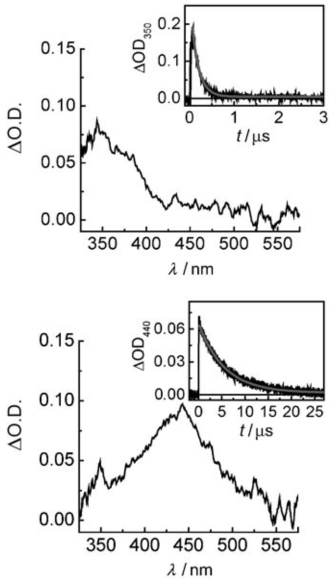


Figure 1. Transient absorption spectra obtained at 200 ns after the 308 nm laser flash photolysis of **1** (top) and **3** (bottom), respectively, in argon-saturated BZ. The insets show the time profiles of transient absorptions obtained at 350 nm for **1** and at 440 nm for **3**. The time profiles were fitted by the first-order decay function (solid line).

On the other hand, the transient absorption peak around 440 nm is characteristic for a 1,4-biradical generated from a Norrish-Type-II hydrogen transfer reaction of the triplet-excited phenyl alkyl ketones.[14,15] Excitation of **5** has been reported to give efficiently 2-methylcyclopropyl phenyl ketone in 90 % yield,[12,16] and excitation of **6** gives efficiently a mixture of cyclization and Norrish-Type-II cleavage products.[17] No transient absorption spectra were detected from **5** during the 308 nm laser excitation; this observation supports the postulated exceedingly fast-reaction, secondary cleavage process.[12] Compared with **1**, the transient absorption band of **6** showed a slight blue shift and shorter lifetime. These laser flash photolysis results of **1**–**6** give strong evidence that the transient absorption spectra of **1**–**4** are not due to the triplet states. Otherwise, the transient absorption spectra of **2**–**4** should be similar to that of **5**, and the transient absorption spectra of **1** should be similar to that of **6**, because of their similar structure. The possibility of other transient species with similar transient absorption spectra is ruled out. Strong evidence for this assumption also came from the 308 nm laser flash photolysis experiments of 2-hydroxyacetophenone in Ar-saturated AN and BZ (Figure S8 in the Supporting Information), in which the transient absorption spectra of 2-hydroxyacetophenone were very similar to that of acetophenone in the T_1 state. It has been reported by Turro et al. that benzoin in the T_1 state has the transient absorption spectrum similar to that of acetophenone in the T_1 state.[18] Consequently, the transient absorption spectra signals at 347 nm for **1** and 440 nm for **2**–**4** are assigned to 1,4-biradicals generated from Norrish-Type-II reactions of **1**–**4** during the 308 nm laser excitation. The lifetimes of the 1,4-biradicals are given in Table 1.

Table 1. Transient absorption measurements during the 308 nm laser flash photolysis of **1**–**6** and AP.[a]

	Substituent at the α-position	Solvent	Lifetime (τ_{BR}) [ns]	Absorption peak [nm]
1	$NHCOCH_3$	BZ[b]	160	345
1	$NHCOCH_3$	AN[c]	450	347
2	OH	BZ	790	441
2	OH	AN	1390	432
3	$OCOCH_3$	BZ	4930	443
3	$OCOCH_3$	AN	1540	435
4	$O(CO)OCH_2CH_3$	BZ	4910	441
4	$O(CO)OCH_2CH_3$	AN	1460	438
5	OSO_2CH_3 (OMs)	BZ	< 25	–
5	OSO_2CH_3 (OMs)	AN	< 25	–
6	$NHCOCH_3$	BZ	< 100	325
6	$NHCOCH_3$	AN	< 100	325
AP	–	BZ	630	326
AP	–	AN	710	330
PP[d]	H	BZ	150	–

[a] AP = acetophenone. [b] BZ = benzene. [c] AN = acetonitrile. [d] PP = propiophenone (reference [3]).

To evaluate the significance of the transient decay analyses, we performed a laser power study with the long-lived transients reported in this manuscript (Figure 2; more details are given in the Supporting Information). For example, in the case of **1** in benzene, the parameters of the first-order exponential fits ($Y = Y_0 + A_1 e^{(-x/t_1)}$) are shown in Table 2, demonstrating that the t_1 values are identical within 10 % error with the variation of the laser power. These experiments were performed under slightly different conditions than those for which the results given Table 1 are based and therefore the t_1 values are about 50 ns longer.

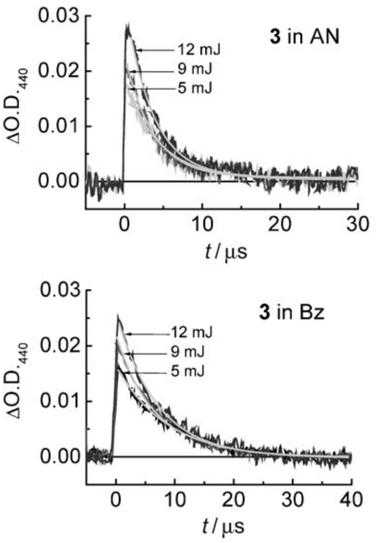


Figure 2. Time profiles of the transient absorption observed at 440 nm during the 308 nm laser flash photolysis of **3** at three 308 nm laser intensities in Ar-saturated AN and BZ. The negative signal in the time region of 0–100 ns is due to the 308 nm laser emission.

Table 2. Laser-power study for compound **1**.

Laser intensity [mJ pulse^{-1}]	Y_0	A_1	t_1 [s]
5	0.00027	0.0575	2.18×10^{-7}
9	0.0	0.0934	2.41×10^{-7}
12	0.0001	0.129	2.12×10^{-7}

The possibility of the occurrence of Norrish-Type-I cleavage in **1**–**6** can also be excluded on the basis of the following three arguments. Firstly, the occurrence of Norrish-Type-I cleavage in **1**–**6** should give the 4-methylbenzoyl (4-$CH_3C_6H_4CO^{\bullet}$) or the benzoyl radical ($C_6H_5CO^{\bullet}$) with an absorption around 325 nm.[19] The molar absorption coefficients of the transient absorption of 4-$CH_3C_6H_4CO^{\bullet}$ and $C_6H_5CO^{\bullet}$ are $\varepsilon_{325}=3700\,\text{M}^{-1}\text{cm}^{-1}$ and $\varepsilon_{325}=3500\,\text{M}^{-1}\text{cm}^{-1}$ ($\varepsilon_{317}=12\,000\,\text{M}^{-1}\text{cm}^{-1}$ of the transient absorption of benzyl radical as the reference).[20] Therefore, the transient absorption of 4-$CH_3C_6H_4CO^{\bullet}$ or $C_6H_5CO^{\bullet}$ can be easily detected, as shown in Figure 3 in which the C–O bond cleavage of benzoic acid α-naphthyl ester (C_6H_5CO-$O^{\alpha}Np$) occurred to give $C_6H_5CO^{\bullet}$ and $^{\alpha}NpO^{\bullet}$ with bsorption peaks around 325 and 397 nm, respectively, during the 266 nm laser flash photolysis of C_6H_5CO–$O^{\alpha}Np$.

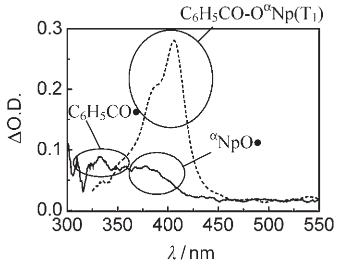


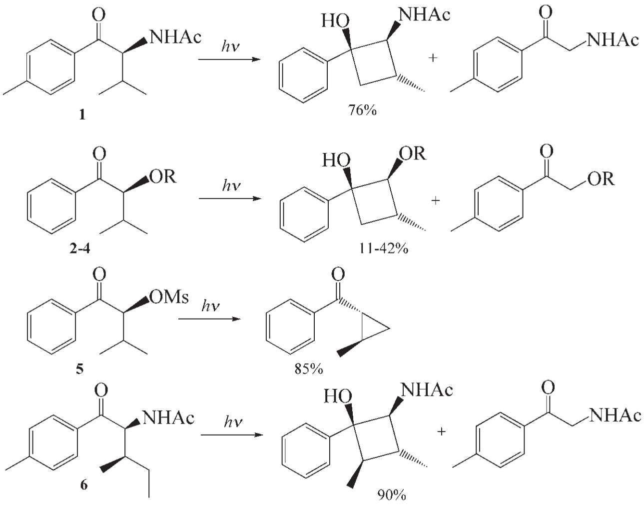
Figure 3. Transient absorption spectra observed during the 266 nm (solid line) and 355 nm (dotted line) laser flash photolysis of benzoic acid α-naphthyl ester (C_6H_5CO–$O^{\alpha}Np$) in Ar-saturated acetonitrile at room temperature.[35]

On the other hand, the transient absorption of C_6H_5CO–$O^{\alpha}Np$ in the triplet excited state ($\varepsilon_{415}=23\,000\,\text{M}^{-1}\text{cm}^{-1}$, with $\varepsilon_{415}=24\,500\,\text{M}^{-1}\text{cm}^{-1}$ of the transient absorption of naphthalene in the triplet state as the reference)[13] was observed with a peak at 415 nm, while no cleavage occurred during the 355 nm laser flash photolysis of C_6H_5CO–$O^{\alpha}Np$ in the presence of benzophenone (BP) used as the triplet sensitizer, as shown in Figure 3. Therefore, in case of a Norrish-Type-I cleavage contribution for **1**–**6**, the absorption band of $ArCO^{\bullet}$ radical around 325 nm could be detected during the laser flash photolysis; the experimental results clearly indicate that no Norrish-Type-I cleavage occurs during the laser flash photolysis of **1**–**6**.

Secondly, if a Norrish-Type-I cleavage were to occur in **1**–**6**, 4,4′-dimethylbenzil or benzil should be obervable as one of the reaction products. We did, however, detect Norrish–Yang as well as Norrish-Type-II cleavage products.[7,8] Thirdly, these results are also consistent with experiments performed by de Mayo and Ramnath on the photochemistry of α-methoxy acetophenones.[21] These compounds preferentially underwent Norrish-Type-II cleavage if no additonal substituent was present at the of α-carbon atom. Norrish-Type-I cleavage was the major reaction pathway only for quaternary substrates or for acetophenones with an additional phenyl group at the α-carbon atom.

Transient lifetimes: The lifetimes of triplet 1,4-biradicals generated from the α-substituted β-methylbutyrophenone derivatives **1**–**4** are in the range 0.2–5 μs; these values are 10–40 times longer than those of non-substituted derivatives.[3] For comparison, a value for the lifetime of the parent 1,4-biradical from butyrophenone of 150 ns in benzene is reported. Thus, the unusually long lifetimes especially for the biradicals from **2**–**4** can be attributed to an α-substituent effect. We assume that the use of the *p*-methylbenzoyl chromophore (conditional on the substrate synthesis) in **1** and **6** does not significantly contribute to the reduced lifetimes of the corresponding intermediates. Although the effects of substituents at the 1- and 4-position of triplet 1-hydroxytetramethylenes have been elucidated,[15,22] there are no reports on such α-substituent effects. Apparently, only the properties of the heteroatom substituent at the 2-position of the triplet biradical leads to these dramatic differences.

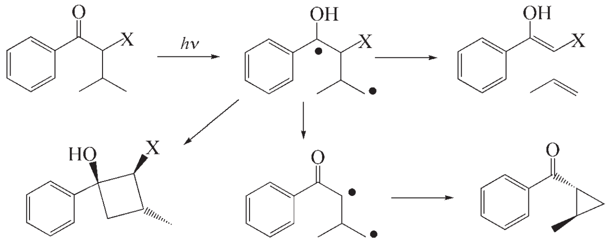
If the lifetimes of these biradicals are determined only by the intersystem crossing (ISC) processes, which are mainly controlled by spin orbit coupling (SOC, that is, $k_{\text{isc}}=1/\tau_{\text{BR}}$),[3,23,24] two major stereoelectronic effects are relevant: substituent influence on the relative angular orientation of the orbitals at the spin-bearing centers C1 and C4 and the degree of overlap between two radical centers. In the present study, the degree of substitution is constant over all substrates (apart from the extra methyl group in **6**). Therefore, we expected a minor influence on the geometries of the intermediate triplet biradicals.[7,8] Inspection of the photochemically produced products (Scheme 1), however, revealed that there is a pronounced substituent effect: α-amido-substituted β-methyl butyrophenones in general (here **1** and **6**) give the Yang cyclization products in good yields, as well as minor amounts of Norrish-Type-II cleavage products.



Scheme 1. Photochemical reactivities (acetonitrile irradiation at 350 nm).

The α-oxy-substituted butyrophenone derivatives **2**–**4** result in lower amounts of cyclobutanols and preferentially give the Norrish-Type-II cleavage products. Finally, the α-mesyloxy compound **5** results in a substituent cleavage/cyclization product.

An appealing interpretation of this product pattern together with the lifetime data is the degree of stabilization of the α-heteroatom-substituted carbon radical center. By increasing the "leaving group ability" of the substituent X at the α-carbonyl position, the negative hyperconjugative interaction between the p orbital at the carbon radical center and the σ* orbital of the C−X bond is increased. This lowers the energy of the α-heteroatom-substituted carbon radical center and also decreases the SOC of the two radical centers in the 1,4-biradicals. Consequentially, hyperconjugative interaction increases the singlet–triplet gap and the triplet 1,4-biradical lifetimes.[25] Assuming the following sequence of σ* acceptor abilities—NHAc $\leqslant$ OH < $O(CO)CH_3$, $O(CO)OCH_2CH_3$—the triplet biradical lifetimes should increase in this sequence (Table 1, 160 ns < 790 ns < 4930, 4910 ns in BZ). This assumption is in agreement with quantum chemical calculation (vide infra). In the case of the even better mesyloxy leaving group, a switch in mechanism is observed and a "spin shift reaction" results in the formation of the 2-methylcyclopropyl phenyl ketone in 90% yield following the excitation of **5**.[12,16] In this case, the lifetime of the triplet biradical intermediate is remarkable short (< 25 ns), because of the rapid elimination at the stage of the triplet biradical (Scheme 2).



Scheme 2. Reaction modes: biradical cleavage, cyclization, elimination.

It has been frequently observed for triplet 1-hydroxytetramethylenes that an increase in solvent polarity leads to a triplet-biradical lifetime increase.[3,23] It has been suggested that hydrogen bonding of the biradical with the solvent modifies the biradical conformation and reduces the ISC rate. Additionally, increasing hydrogen-bonding between the solvent and the biradical is expected to slow down the hydrogen back-transfer process.[3,16] This solvent effect is apparent for substrates **1** and **2**, for which τ_{BR} increased from 160 to 450 ns and from 790 to 1390 ns, respectively, when going from benzene to acetonitrile. In contrast, with substrates **3** and **4**, the τ_{BR} values decreased from 4930 to 1540 ns and 4910 to 1460 ns, respectively, when changing the solvent from benzene to acetonitrile. This indicates that the long lifetimes for the triplet biradicals **3** and **4** in benzene are in part a consequence of intramolecular stereoelectronic effects, which are attenuated in more polar medium. The assumption of stereoelectronic effects are in accord with theoretical calculations (vide infra) and are expected to slow down bond rotations in the biradical that are necessary to reach optimal geometries for intersystem crossing and subsequent product formation.[26,27]

The amido group is an excellent hydrogen-bond acceptor, actually the best in the row NHAc, OH, OAc, and O(CO)OEt. Thus, intramolecular hydrogen-bonding at the stage of the triplet 1,4-biradical was postulated by us as the decisive interaction, which 1) directs the reaction path into the cyclization channel by "freezing" the precyclization conformation and 2) maximizes the diastereoselectivity of the cyclobutanol formation due to this conformational fixation.[7] When going to weaker hydrogen-bonding acceptor groups, the cyclization efficiency decreased and also, to a lesser extent, the diastereoselectivity. In Table 3 the quantum yields for product formation for the α-amido- with the α-oxy-substituted butyrophenone derivatives **1**,[8] **3**, and **4** are compiled. Whereas only a slight increase in the total

Table 3. Quantum yields for photoprocesses of **1**, **3**, **4**.[a]

Substrate	Φ_t	Φ_c	Φ_f
1[8]	0.21	0.19	0.02
3	0.30	0.09	0.21
4	0.34	0.15	0.19

[a] In benzene, ±0.02, by valerophenone actinometry; t = total, c = cyclization, f = fragmentation.

product formation quantum yield Φ_t appears, the fragmentation path (Φ_f) is increased by a factor of ten.

The solid-state structures of α-heteroatom-substituted butyrophenones (e.g., **5** see Figure 4),[28] indicated that there is a stereoelectronic preference for the *syn*-periplanar arrangement of the α–CX bond with the carbonyl group. From this geometry, however, the hydrogen transfer cannot occur and bond rotation has to precede the Norrish-Type-II process. To stabilize the benzylic radical center formed by γ-hydrogen transfer, in case of the less effective hydrogen-bond acceptors, OAc and O(CO)OEt, a staggered conformation of the 1,4-biradicals with antiperiplanar C–O-bonds is likely.

Table 4. UB3LYP/6–31G* computed model structures **A**–**D** with relative energies and NBO donor (SOMO)–acceptor (σ*) interactions.[a]

	Coplanar	Perpendicular
A, $X = NH_2$		
E_{rel} [kcal mol^{-1}]	+1.5	0.0
NBO [kcal mol^{-1}]	SOMO →σ* C–N: 8.1	SOMO →σ* C–H: 5.3
B, X = NH–C(=O)H (NH-formyl)		
E_{rel} [kcal mol^{-1}]	0.0	+0.8
NBO [kcal mol^{-1}]	SOMO →σ* C–N: 8.7	SOMO →σ* C–H: 5.0
C, X = OH		
E_{rel} [kcal mol^{-1}]	0.0	+0.8
NBO [kcal mol^{-1}]	SOMO →σ* C–O: 10.1	SOMO →σ* C–H: 5.3
D, X = O–C(=O)H (O-formyl)		
E_{rel} [kcal mol^{-1}]:	0.0	+1.7
NBO [kcal mol^{-1}]	SOMO →σ* C–O: 12.6	SOMO →σ* C–H: 5.1

[a] UB3LYP/6–31G* optimized structures, ZPE were scaled by 0.9806.

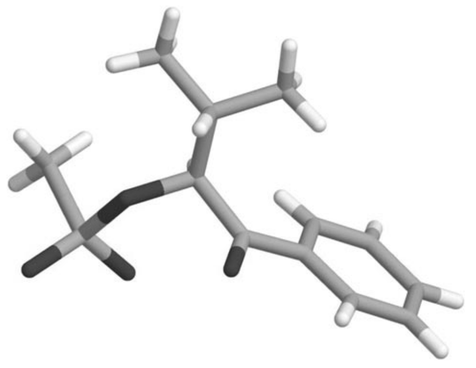


Figure 4. Structure of the mesylate **5** in the crystal.

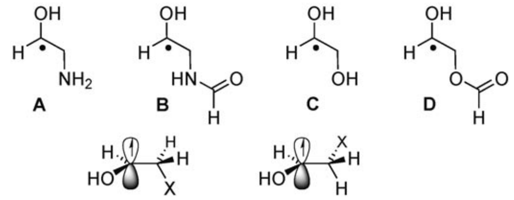


Figure 5. UB3LYP/6–31G* computed model structures with coplanar and perpendicular C–X moieties.

Computational results and methods: To analyze stabilization effects in nucleophilic α-hydroxy radicals[29] with varying N and O substituents in the β-position, UB3LYP/6–31G*[30] and natural bond orbital (NBO) analyses[31] were performed on the model β-nitrogen-substituted radicals **A** and **B** as well as for the β-oxygen-substituted radicals **C** and **D**. As it is apparent from relative energies ($E_{rel.}$) of coplanar versus perpendicular C–X conformations in **A**–**D**, the coplanar arrangements become more favored with increased σ* C–X acceptor abilities in the order $X = NH_2 <$ NH-formyl ≈ OH < O-formyl. In agreement, the SOMO (donor) σ* C–X acceptor interactions of coplanar arrangements increase in the same order and point to strongest radical stabilizations through negative hyperconjugation[32] with β-positioned O-formyl (12.6 kcal mol^{-1}) and OH (10.1 kcal mol^{-1}) groups (Table 4 and Figure 5).[33]

This arrangement imprints a zwitterionic contribution to the 1,4-biradical (Figure 6), which might explain the increase in triplet lifetime.[23] Such zwitterionic character of the triplet 1,4-biradicals may be responsible to the difference of the absorption peaks between AN and BZ (Table 1). In the polar solvent (AN) the zwitterionic character makes a greater contribution, and the absorption peak shows a blue shift relative that found in the nonpolar solvent (BZ).

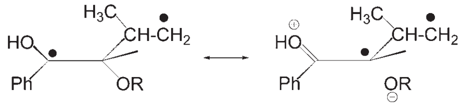


Figure 6. 1-Hydroxytetramethylene biradicals with zwitterionic contribution.

In conclusion, a remarkable effect of substituents at the α-carbonyl position upon the lifetimes of triplet 1,4-biradicals generated from Norrish-Type-II reaction is observed. The σ* acceptor ability of the substituent at the α-carbonyl position has a serious consequence on the rate of intersystem crossing. The lifetimes of these 1,4-biradicals are almost 10–40 times longer than those of unsubstituted compounds. Whereas interactions with polar solvents lead to an increase in biradical lifetimes for the unsubstituted or α-amido-substituted cases, α-oxy-substituted 1-hydroxytetramethylenes are destabilized in the presence of polar solvents.

Experimental Section

The samples of **1**–**6** were prepared according to procedures described in references [7,8]. Acetophenone was purchased from Nacalai Tesque Inc. and recrystallized twice from ethanol before use. Acetonitrile (spectral grade) and benzene (spectral grade) were purchased from Nacalai Tesque Inc. and used directly. Sample solutions were freshly prepared and deoxygenated by bubbling with argon (Ar) gas before irradiation. All experiments were carried out at room temperature.

The laser flash at 308 nm (5 mJ pulse^{-1}, 25 ns) was obtained from a XeCl excimer laser (Lambda Physik, COMPex). The probe light was obtained from a 450 W Xe-lamp (Osram XBO-450). The probe beam was passed through an iris with a diameter of 0.3 cm and sent into the sample with a perpendicular intersection of the laser beam. The probe beam was then focused on a monochromator (Nikon G250). The output of the monochromator was monitored using a PMT (photomultiplier tube; Hamamatsu Photonics R928). The signal from the PMT was recorded on a transient digitizer (TDS 580D four channel digital phosphor oscilloscope, 1 GHz, Tektronix). A Hamamatsu Photonics multichannel analyzer (C5967) system was used for measurement of the transient absorption spectra. The whole system was controlled with a personal computer by means of a GP-IB interface. To avoid any damage of the sample solution by the probe light, a suitable cutoff filter was used in front of the sample.

The quantum yields for the photodecomposition of substrates **3** and **4** were determined by using a merry-go-round apparatus with valerophenone as an actinometer.[34] The product composition was measured as a function of time by gas chromatography and the total quantum yields Φ_T for substrate photodecomposition were separated into quantum yields for cyclization Φ_C and quantum yields for Norrish-Type-II fragmentation Φ_F from the total product analysis after complete conversion.

Acknowledgements

This work has been partly supported by a Grant-in-Aid for Scientific Research (Project 17105005, Priority Area (417), 21st Century COE Research, and others) from the Ministry of Education, Culture, Sports, Science and Technology (MEXT) of Japanese Government, and Deutsche Forschungsgemeinschaft.

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Received: January 4, 2006