Photoreactions of Biacetyl with Electron-rich Olefins. An Extended Mechanism[1]

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The photoreactions of biacetyl (**1**) with various electron-rich olefins have been investigated. Oxetanes and allyl alcohols are formed upon irradiation with λ = 400–480 nm ($n\pi^*$ excitation of biacetyl) depending on the nature of the olefin. An unusual relationship between the rate constants of luminescence quenching of biacetyl by olefins (log k_q) and the free enthalpies of electron transfer (ΔG_2) indicate formation of an exciplex first. A reasonable good fit between experimental results of log k_q and ΔG_2 has been obtained on the basis of a mechanistic model which includes the exciplex intermediate as well as an ionic photodissociation pathway and some empirical adjustment of the parameters. Complete electron transfer as a consecutive process has been proven for some strong electron-donating olefins by means of ESR spectroscopy and scavenging of the radical cations. The solvent dependence of the product quantum yields further confirms the competition between ionic photodissociation and product formation. The preferred formation of allyl alcohols (reduction products) with strong electron-donating olefins and the highly regioselective oxetane formation with ketene acetal are discussed in terms of exciplexes of strong CT character or even contact ion pairs and dipolar intermediates.

Photoreaktionen von Biacetyl mit elektronenreichen Olefinen. Ein erweiterter Mechanismus[1]

Die Photoreaktionen von Biacetyl (**1**) mit verschiedenen elektronenreichen Olefinen wurden untersucht. Im allemeinen bilden sich bei der Bestrahlung mit λ = 400–480 nm ($n\pi^*$-Anregung von Biacetyl) in Abhängigkeit von der Olefin-Struktur Oxetane und Allylalkohole. Hinweise auf die primäre Bildung eines Exciplexes liefert die ungewöhnliche Abhängigkeit der Geschwindigkeitskonstanten der Lumineszenzlöschung von Biacetyl durch die Olefine (log k_q) von der freien Bildungsenthalpie des Elektronentransfers (ΔG_2). Ein Mechanismus mit einer Exciplex-Zwischenstufe und einem ionischen Photodissoziationsweg gestattet es nach Anpassung der Parameter, die experimentellen Daten gut zu simulieren (log $k_q/\Delta G_2$-Korrelation). Vollständiger Elektronentransfer wurde als Folgeprozeß bei einigen besonders elektronenreichen Olefinen mit Hilfe der ESR-Spektroskopie bzw. durch Abfangen der Radikalkationen bewiesen. Die Abhängigkeit der Produktquantenausbeuten von der Lösungsmittelpolarität bestätigt die Konkurrenz zwischen Produktbildung und ionischer Photodissoziation. Die bevorzugte Bildung von Allylalkoholen (Reduktionsprodukte) mit starken Donor-Olefinen und die regioselektiv ablaufende Oxetanbildung mit Ketenacetal werden auf der Basis von stark polaren Exciplexen bzw. Kontaktionenpaaren und Zwitterionen als Zwischenstufen diskutiert.

Photoreactions of electronically excited carbonyl compounds with olefins have been extensively studied from the early beginning of photochemistry[2]. In general the products are [2 + 2] cycloadducts (oxetanes), allyl and enol ethers (ene-type adducts), and, in fewer cases, allyl alcohols (reduction products), formed by abstraction of an allylic hydrogen from the olefin by the excited carbonyl compounds and recombination of the two resulting radicals. This reaction pattern also holds for 1,2-diketones including the additional formation of [4 + 2] cycloadducts (dihydrodioxines) which have been the subject of several investigations starting from the early report of Schönberg and Mustafa[3] up to, for example, Cerfontain[4], Turro[5], Jones[6], Carless[7], and others[2,8], including our own preliminary work[9].

In particular photoreactions of biacetyl (**1**) with olefinic compounds[10] like 2,3-dimethyl-2-butene[4–6], ethyl vinyl ether[6,11], furan[6,11], indene[6,11], and other simple alkenes[4] do not show extremely high selectivities – even though the selectivities are higher than those of similar reactions with acetone[12,13]. Exceptions are symmetrical olefins like 1,2-dimethoxyethene[6] which do not contain allylic hydrogen and β,β-disubstituted vinyl ethers which at least form regioselectively 2-alkoxyoxetanes[7]. Generally, exciplexes and 1,4-biradicals are proposed as intermediates[2,4]. At least the relatively low regioselectivities of these photoreactions especially in case of simple ketones can be viewed in terms of this exciplex-biradical model[2] indicating too small stability differences of the differently substituted biradicals **A** and **B**, respectively (Scheme 1).

According to Weller[14] both locally excited states and charge transfer configuration contribute to the exciplex state formed by excitation of electron donor (D) and acceptor (A) molecules:

$$A^*D \longleftrightarrow AD^* \longleftrightarrow A^{\cdot -}D^{\cdot +} \qquad (1)$$

The CT character of exciplexes can be estimated by Weller's theory of electron transfer[15]. Using this procedure (see below) all the above cited olefins[4–6,11] cause a relatively small charge separation upon photolysis in the presence of **1** as electron acceptor. This further supports the exciplex-biradical mechanism. Stronger electron-donor olefins than those previously used are 1,3-dioxoles (**2**), now easily accessible according to a method developed in our laboratory[16]. At least methyl-substituted derivatives of **2** are expected to give almost exergonic electron-transfer processes with **1**[9c]. Even the poorest donor, 1,3-dioxole (**2a**), should form an exciplex of extreme CT character which may further dissociate into solvated radical ions in solvents of high polarity. As a consequence we have investigated in detail the interaction of biacetyl (**1**) with a variety of electron-rich olefins **2**–**6** (Scheme 2) in order to check the possibility of an electron transfer experimentally and further to gain

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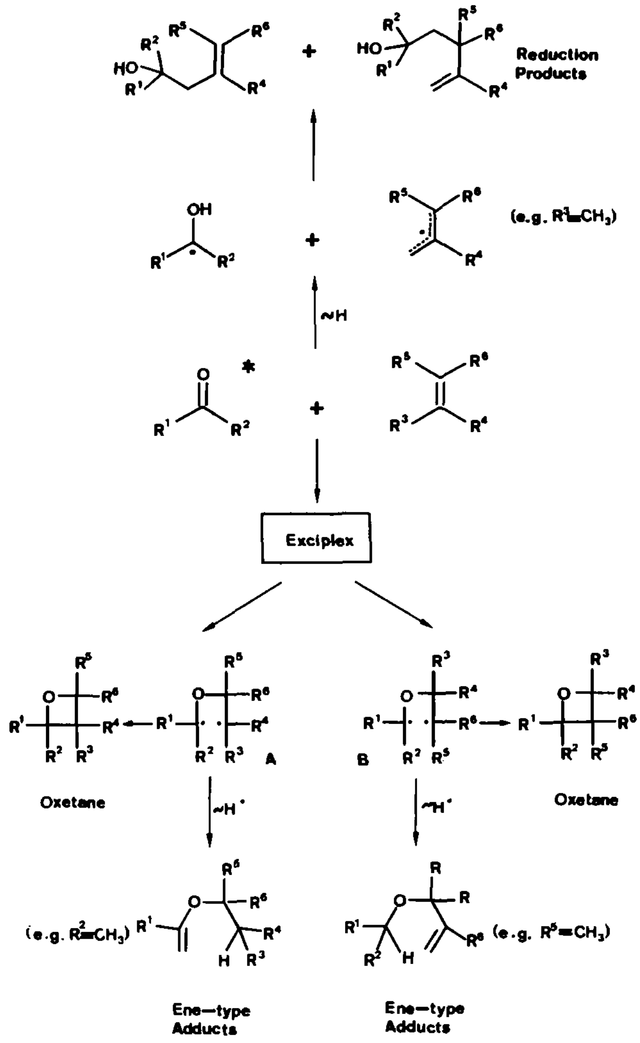
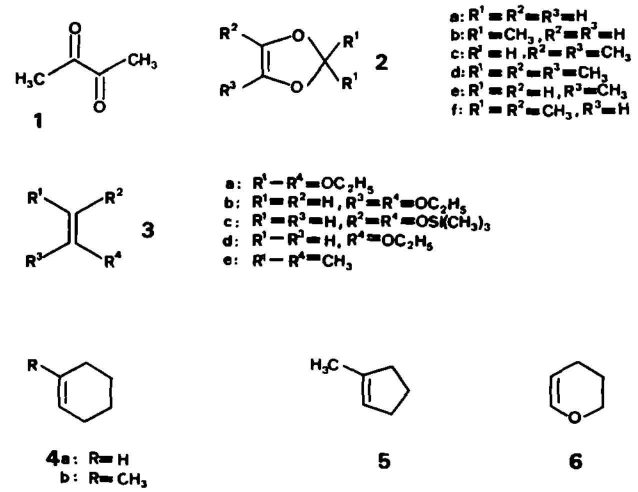
some insight to the effect of charge transfer on the selectivity of these photoreactions. Especially a study with the unsymmetrically substituted 1,1-diethoxyethene (**3b**) should provide informations about the effect on the regioselectivity.

Scheme 1. Products of photoreactions of ketones with olefins



Scheme 2



We expect from these investigations not only a deeper understanding of the charge transfer-selectivity relationship but also a stimulation for synthetic applications. Just recently the Paterno-Büchi reaction has become a powerful tool in modern organic synthesis[2,17,18].

1. Results

1.1. Preparative Reactions. Isolation and Identification of Products

Biacetyl (**1**) and 1,3-dioxoles **2a–d** gave two principal products in 50–70% yields upon photolysis in benzene or cyclohexane with λ = 400–480 nm; i.e., **7–9** from cycloaddition and **10–12** from reduction (Scheme 3). The ratio of these products strongly depends on the structure and the donor abilities of **2**:

(1) Only dioxoles **2** containing allylic hydrogen form reduction products.

(2) Increasing alkyl-substitution of **2** (that means decreasing oxidation potential $E_{1/2}^{\text{Ox}}$ – see below) results in increasing reduction product formation, e.g., $\Phi_{\text{reduction}}/\Phi_{\text{addition}}$ = 0.07/0.08 [0.22/0.02] for **1** + **2c** [**2d**].

(3) The 1,4-addition to dioxenes is only observed with **2a** and occurs up to about 1/3 of the total product mixture (**7a**:**8a**:**9** = 1.2:1.0:1.1).

The products were isolated both by preparative GC and HPLC. The latter proved to be the better method. All these purified products were identified as 1:1 adducts according to spectral analyses (^{1}H and ^{13}C NMR, IR, MS). NOE experiments confirm the *exo*- and *endo*-configuration of **7a** and **8a**, respectively. Further structural evidence was obtained from the conversion of the products from **2d** and **2b** into the ketals **13**, **14a** and **14b**, respectively.

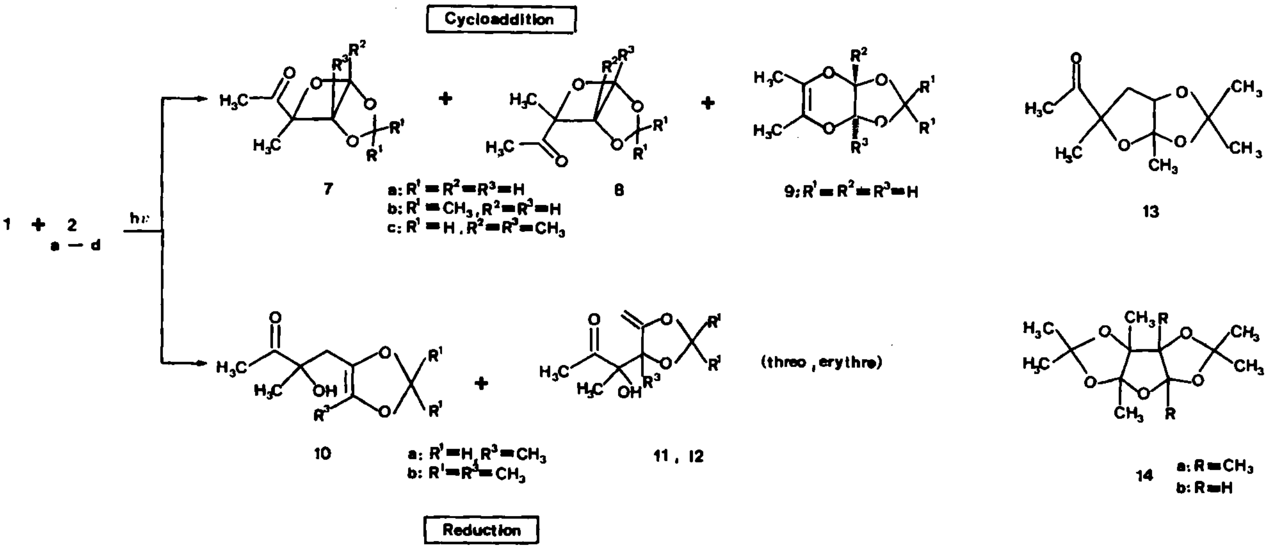
Preparative irradiation of 1:1 mixtures containing **1** and 1,1-diethoxyethene (**3b**) under similar conditions but in diluted benzene or cyclohexane solutions results in the formation of only one cycloadduct **15** in 69% yield. **15** was easily identified as 2-acetyl-3,3-diethoxy-2-methyloxetane by means of IR, ^{1}H- and ^{13}C-NMR analyses. In contrast to this photoaddition the thermal reaction of **1** and **3b** in polar solvents like acetonitrile at room temperature yields exclusively the other regioisomer **16** in 34% yield beside some acyclic 1:1 and 1:2 adducts of the aldol-type[6b,19].

The photochemical and thermal reactions of **1** and **3b** are totally complementary and therefore represent an example for a photochemically induced "Umpolung" of the reactivity of 1,2-diketones. Since both reactions compete with each other, the photoaddition only proceeds in a clean way under diluted conditions (<0.1 M), i.e. in an unpolar reaction medium.

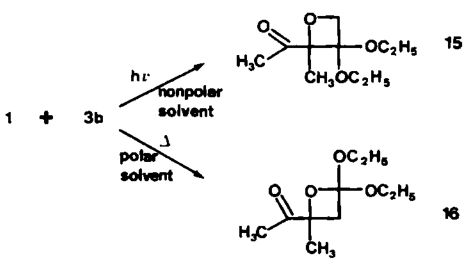
1.2. Luminescence Quenching, Reactive States of Biacetyl, and Correlation with Oxidation Potentials of Donor Olefins

The room-temperature fluorescence and phosphorescence of argon-purged solutions of **1** in various solvents were quenched with varying efficiency on addition of the olefins **2–6**. The oxidation potentials of the olefins are listed in Table 1 along with the quenching data obtained from Stern-Volmer analysis. The fluorescence lifetime τ_F in benzene was measured by means of single-photon counting technique.

Scheme 3. Products of photoreactions of biacetyl (**1**) with 1,3-dioxoles **2**



Scheme 4. Photochemical and thermal cycloaddition of biacetyl (**1**) to 1,1-diethoxyethene (**3b**)



The triplet lifetimes were calculated from the ratio of phosphorescence to fluorescence maxima (P/F ratio). The calibration was carried out by measuring the phosphorescence lifetimes τ_P by means of flash-spectroscopy in dependence on the P/F ratio (for phosphorescence lifetimes of pure biacetyl see Table 2) – the details are described elsewhere[20].

Both from these data and from the product quantum yields (see below) it is concluded that only **1** and **2d** react in a "clean" S_1 reaction at concentrations >0.3 mol/l (fluorescence quenching >97%, $\Phi_P = 0.24$). The portion of a T_1 reaction increases with decreasing quenching rate con-

Table 1. Oxidation potential of olefins and Stern-Volmer data for quenching of biacetyl (1) luminescence

				k_q [M^{-1} s^{-1}][c]	
Olefin	$E_{1/2}^{Ox}$[a] [V]	F/P[b]	Acetonitrile	Benzene	Cyclohexane
4a	1.72	P	$(3.75 \pm 0.07) \times 10^5$		
4b	1.47	P	$(8.45 \pm 0.54) \times 10^5$		
3d	1.44	P	$(1.83 \pm 0.19) \times 10^6$		
5	1.40	P	$(1.61 \pm 0.07) \times 10^6$		
3e	1.21	P	$(2.54 \pm 0.07) \times 10^6$		
6	1.16	P	$(4.76 \pm 0.02) \times 10^6$		
3b	0.85	P	$(8.45 \pm 0.61) \times 10^6$	$(1.39 \pm 0.10) \times 10^7$	$(6.77 \pm 0.61) \times 10^6$
		F	$(2.64 \pm 0.13) \times 10^8$	$(3.67 \pm 0.09) \times 10^8$	
3c	0.77	P	$(3.94 \pm 0.10) \times 10^7$		
2a	0.76	P	$(2.44 \pm 0.23) \times 10^7$	$(6.65 \pm 0.59) \times 10^7$	$(2.22 \pm 0.19) \times 10^7$
		F	$(1.01 \pm 0.04) \times 10^9$	$(4.90 \pm 0.22) \times 10^8$	
2b	0.69	P		$(1.13 \pm 0.10) \times 10^8$	
		F	$(1.77 \pm 0.06) \times 10^9$	$(2.44 \pm 0.16) \times 10^9$	
2e	0.60	P	$(2.14 \pm 0.09) \times 10^8$		$(1.94 \pm 0.15) \times 10^8$
		F		$(2.64 \pm 0.14) \times 10^9$	
2f	0.55	P		$(4.88 \pm 0.37) \times 10^8$	
2c	0.48	P		$(1.12 \pm 0.08) \times 10^9$	
		F	$(5.22 \pm 0.67) \times 10^9$		
2d	0.42	P		$(1.79 \pm 0.17) \times 10^9$	
		F	$(4.36 \pm 0.11) \times 10^9$	$(1.06 \pm 0.08) \times 10^{10}$	
3a	0.32	F	$(4.73 \pm 0.21) \times 10^9$		

[a] Oxidation potentials were measured by cyclic voltametry versus Ag/AgNO₃. – [b] F: Fluorescence Quenching; P: Phosphorescence Quenching. – [c] Argon-purged solutions at 20°C (see ref.[20]). For phosphorescence lifetimes see Table 2. Fluorescence lifetime $\tau_F = 9.15 \pm 0.20$ ns by single-photon counting technique (see also Turro[21]: $\tau_F = 9.9-10.2$ ns).

Table 2. Lifetimes of biacetyl (**1**) phosphorescence

Solvent	τ_P [µs] This Work[a)]	Literature
Benzene	283.6 ± 15.4[b)]	135[e,4)] 178 – 644[23)] 460 – 560[21a)]
Cyclohexane	180.2 ± 11.7[c)]	
n-Hexane		336[4)]
Acetonitrile	358.4 ± 10.4[d)]	145[4)] 200[21a)]

[a)] Argon-purged solutions at 20°C: c (**1**) = 0.2 M. – [b)] P/F ratio = 16.7 ± 0.6, – [c)] P/F ratio = 10. – [d)] P/F ratio = 13.9 ± 0.7. – [e)] P/F ratio = 12.

stants, e.g. **1** and **3b** react in a "clean" T_1 reaction at concentrations <5 mmol/l (fluorescence quenching <1.6%, $\Phi_P = 0.1$). Both the S_1 and T_1 of biacetyl exhibit the same reactivity, i.e. the same products were formed in the same ratio upon irradiation by varying the concentration of **2a** and **2d**, respectively, from 0.05 to 500 mmol/l. Further evidence was obtained from sensitization experiments using benzophenone: appropriate concentrations of benzophenone, **1** and **2** were chosen according to absorption and emission quenching measurements to ensure only excitation of benzophenone and only triplet-energy transfer to **1**. The product analyses in comparison to the experiments under direct irradiation of **1** were performed by GC. In all cases there was no change in the product formation and the product ratio[22)].

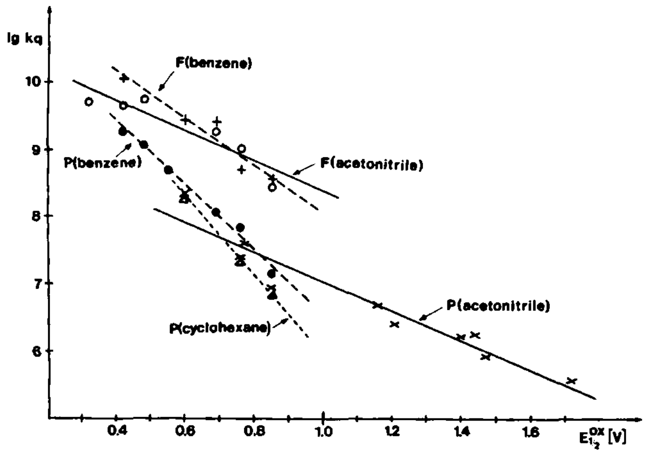


Figure 1. Rate constants for quenching of biacetyl (**1**) luminescence as a function of oxidation potential of quenchers. P/F = quenching of phosphorescence/fluorescence; x/o = P/F in acetonitrile; ●/+ = P/F in benzene; Δ = P in cyclohexane. log $k_q = a + b\ E^{Ox}_{1/2}$, r = correlation coefficient.
Acetonitrile, P: $a = 9.19 \pm 0.26$, $b = -2.16 \pm 0.22$, $r = -0.9615$;
F: $a = 10.59 \pm 0.30$, $b = -2.22 \pm 0.49$, $r = -0.9158$.
Benzene, P: $a = 11.31 \pm 0.16$, $b = 4.76 \pm 0.25$, $r = -0.9944$;
F: $a = 11.55 \pm 0.39$, $b = -3.51 \pm 0.58$, $r = -0.9617$.
Cyclohexane, P: $a = 11.80 \pm 0.02$, $b = -5.84 \pm 0.03$, $r = -0.9999$.

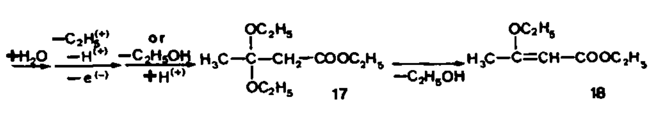
The data of Table 1 already indicate a dependence of the quenching-rate constants on the electron-donor properties of the olefins. In Figure 1 the linear correlations between the rate constants (log k_q) and the oxidation potentials ($E^{Ox}_{1/2}$) are shown. We have chosen the correlation with $E^{Ox}_{1/2}$ rather than with the ionization potential (IP) for several reasons: (i) The fit between log k_q and IP yields a correlation coefficient of only 0.66. Contrary to that the correlation with $E^{Ox}_{1/2}$ is definitely linear (Figure 1). (ii) The oxidation potential can be directly used in the Rehm-Weller equation (eq. 2). (iii) The oxidation potentials include free enthalpies of solvation. (iv) Last not least the oxidation potentials are easier to measure. Our systems show a ca. 2 – 3 fold stronger CT character of luminescence quenching than systems of simple ketones/enol ethers[24)] and α-trifluoroacetophenone/alkylaromatics[25)], which are supposed to exhibit only small contributions of charge transfer in the exciplexes. However, Figure 1 exhibits slopes of max. 1/3 of that expected for full electron transfer, i.e. slopes are -2.2 up to $-5.8\ V^{-1}$ for phosphorescence quenching and -2.2 up to $-3.5\ V^{-1}$ for fluorescence quenching compared to $-17\ V^{-1}$ in electron-transfer processes reported by Weller[14a)]. Furthermore there are only small effects on solvent polarity. These results clearly demonstrate that full electron transfer does not occur in this primary step of luminescence quenching.

1.3. ESR Measurements and Scavenging of Free Radical Ions

In order to check the possibility of full electron transfer ESR measurements under in situ photolysis conditions[26)] were undertaken. Contrary to investigations of the photooxygenation of dihydrodioxines via 9,10-dicyanoanthracene-sensitized electron transfer processes by Schaap[27)] and transient absorption measurements of the benzophenone-dihydrodioxine system by Peters[28)] we were able to observe both the radical anion and the radical cations during photoreactions of **1** with **2d** and **2f**, respectively, in acetonitrile simultaneously (Figure 2). In all other reactions of **1** with **2** and **3b** only the semidione radical anion $1^{\overline{\cdot}}$ was detected by means of ESR due to the short lifetimes of the corresponding radical cations[29,30)]. However, the signal intensity of $1^{\overline{\cdot}}$ increases by addition of the electron-donor olefins. These experiments strongly support the involvement of dissociation into free radical ions as an additional reaction pathway in photoreactions of **1** with **2** and **3b**.

Additional evidence for ionic photodissociation was obtained from scavenging experiments in the **1** – **3b** system, which were carried out with 1,1-diethoxyethene (**3b**) itself as scavenger for free radical cations:

Scheme 5. Formation of "dimerization" products from 1,1-diethoxyethene (**3b**) via radical cations



Sens = p–NCC₆H₄CN, **1**

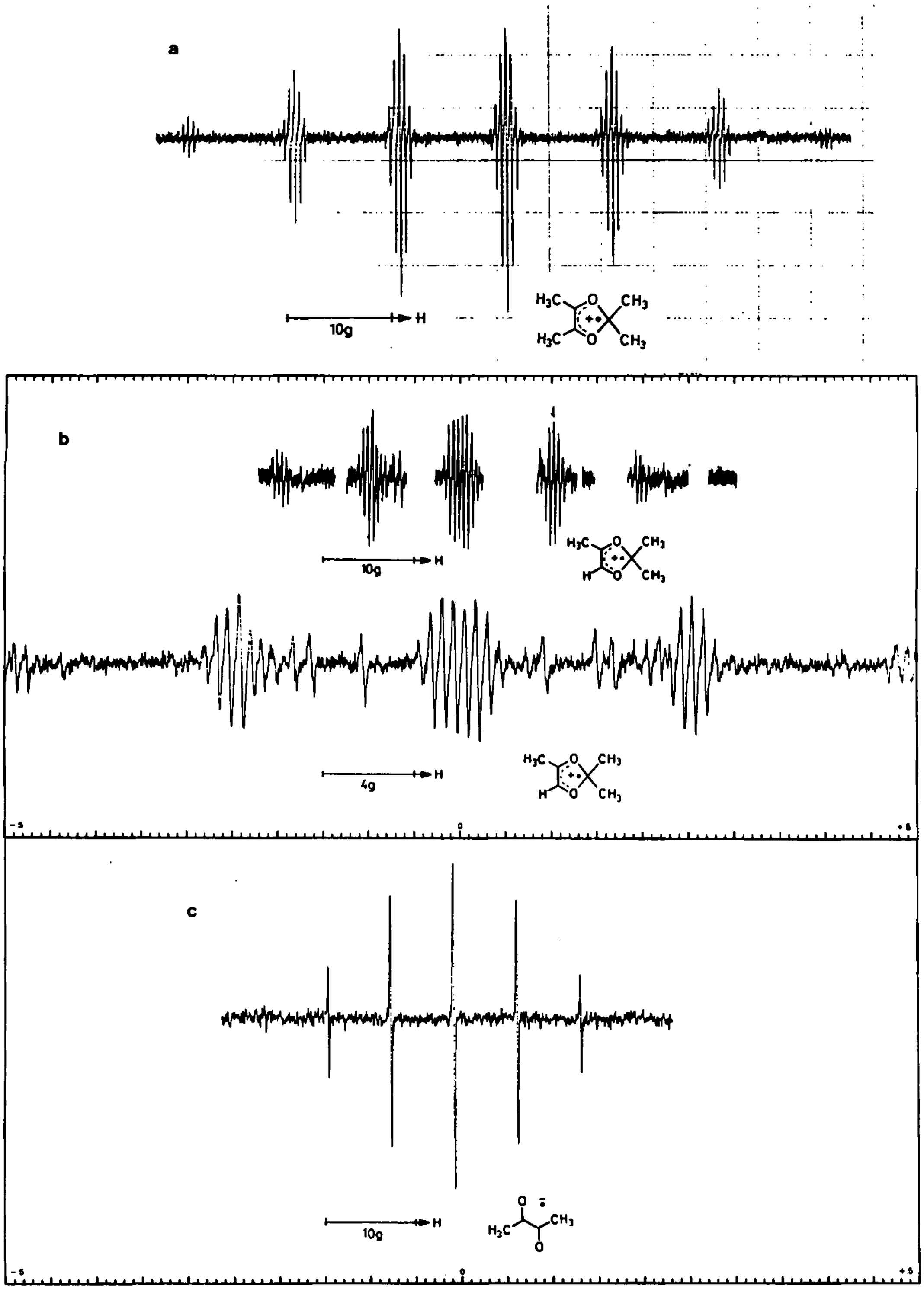


Figure 2. ESR-spectra of radical ions recorded under in-situ photolysis conditions of
a: **2d**, a^H_β = 10.20 G, a^H_γ = 0.47 G
b: **2f**, a^H_α = 10.90 G, a^H_β = 9.50 G, a^H_δ = 0.50 G
c: **1**, a^H = 6.9 G

Besides the oxetane **15** the products **17** and **18** were isolated after photolysis of **1** and **3b** in acetonitrile using HPLC. **17** and **18** were also formed by electron transfer sensitization of **3b** in polar solvents (like acetonitrile or tetrahydrofuran) via a radical-ion mechanism[31] (Scheme 5). Both adducts were identified as dimerization products of **3b** by comparison with an authentic sample[32,33].

1.4. Solvent Dependence of Product Formation and Free Enthalpies of Ionic Photodissociation

All photoreactions of **1** with the olefins **2a**–**d** and **3b** show significant solvent dependences, i.e. the quantum yields of product formation decrease with increasing solvent polarity. Two examples are shown in Table 3 and Figure 3. Moreover, the absolute decrease depends on the donor abilities of the olefins (see Table 1 for oxidation potentials): Φ(cyclohexane/Φ(acetonitrile) = 2.3, 2.3, 2.1, 1.9, and 1.8 for **2d**, **2c**, **2b**, **2a**, and **3b**, respectively.

The system **1** + **2c** was chosen to investigate the influence of solvent polarity on the reduction-cycloaddition ratio since here both reaction modes occur to almost equal amounts.

A small but significant effect was found: Φ(benzene)/Φ(acetonitrile) = 2.4 for formation of **10a**–**12a** (reduction) and 1.9 for formation of **7c**, **8c** (cycloaddition). It should be noted that the photoreactions of **1** with less electron-rich olefins do not show such a solvent dependence.

$$\Delta G_2(\mathrm{A}^{-\cdot}_{s}\ \mathrm{D}^{+\cdot}_{s}) = F[E^{\mathrm{Ox}}_{1/2}(\mathrm{D}) - E^{\mathrm{Red}}_{1/2}(\mathrm{A})] - \Delta E_{\mathrm{excit}} + \Delta E_{\mathrm{coul}} \qquad (2)$$

$$\Delta E_{\mathrm{coul}} = \frac{e^2 N}{4\pi\varepsilon_0 a}\left[\frac{1}{\varepsilon} - \frac{2}{37.5}\right] \qquad (3)$$

Weller's theory of electron transfer[14] provides a method to calculate the free enthalpies of radical ion-pair formation from electron-donor and acceptor molecules by means of equations (2) and (3) simply by using the oxidation potential of the donor, the reduction potential of the acceptor (both in acetonitrile), and the excitation energy ($\Delta E_{\mathrm{excit}}$ in kJ/mol) of the electronically excited species. The term ΔE_{coul} represents the Coulomb interaction energy gained by bringing the two radical ions to the encounter distance a in a solvent of dielectric constant ε [equation (3): F = 96490 C, e = 1.602×10^{-19} C, $\varepsilon_0 = 8.854 \times 10^{-12}$ Fm^{-1}, ε = dielectric constant of solvent, ε of acetonitrile = 37.5, N = 6.023×10^{-23} mol^{-1}, a = 7 Å]. These equations have been successfully applied for various systems as shown in fundamental studies by Weller[14] and Mataga[35] and by others[15,36–38] in empirical correlations with mode selectivities of photoreactions. The results of such calculations are also shown in Table 3 and Figure 3 for the reactions of **1** with **2d** and **3b**. They clearly show parallel curves for both the SSIP formation and the product quantum yields: That means, as ΔG_2 of ionic photodissociation decreases, the quantum yields of product formation are reduced as well. Moreover, for the **1**/**2d** system ionic photodissociation becomes exergonic in solvents with ε > 3 (S_1 reaction, see chapter 1.2). Since the corresponding Φ_P curve also falls off in this ε region a competition between product formation and ionic photodissociation may rationalize these solvent effects. In general the **1**/**3b** system behaves similar. For a T_1 reaction (see chapter 1.2) ionic photodissociation still remains endergonic. However, in acetonitrile a very small ΔG_2 value

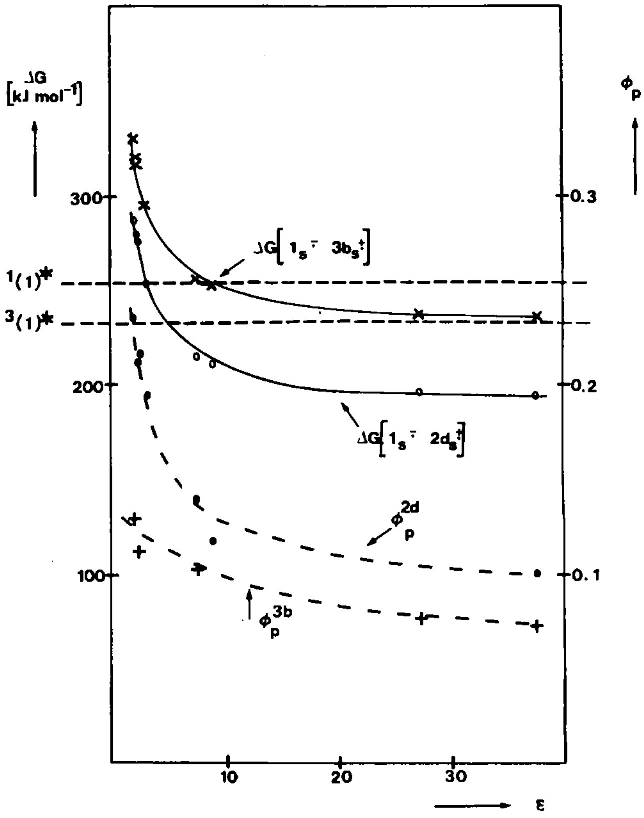


Figure 3. Dependence of free enthalpies of SSIP formation and product quantum yields on solvent polarity. $[\mathbf{1}^{-\cdot}_{s}\ \mathbf{2d}^{+\cdot}_{s}]$ and $[\mathbf{1}^{-\cdot}_{s}\ \mathbf{3b}^{+\cdot}_{s}]$ = SSIP (solvent separated ion pairs), Φ_P^{2d} $[\Phi_P^{3b}]$ = quantum yields of formation of **10b** + **11b** + **12b** [15].

Table 3. Free enthalpies of radical ion pair formation (SSIP) and product quantum yields of photoreactions of biacetyl (**1**) with 2,2,4,5-tetramethyl-1,3-dioxole (**2d**) and 1,1-diethoxyethene (**3b**) in various solvents

Solvents	ε	ΔE_{coul}[a)] [kJ/mol]	$[\mathbf{1}^{-\cdot}_{s}\ \mathbf{2d}^{+\cdot}_{s}]$[b)] ΔG_2 [kJ/mol]	$\Delta G_2 - \Delta E_{\mathrm{excit}}$ [kJ/mol]	$[\mathbf{1}^{-\cdot}_{s}\ \mathbf{3b}^{+\cdot}_{s}]$[c)] ΔG_2 [kJ/mol]	$\Delta G_2 - \Delta E_{\mathrm{excit}}$ [kJ/mol]	Φ_P^{2d}	Φ_P^{3b}
Cyclohexane	2.02	87.7	288.4	+33.7	329.9	+96.3	0.236	0.131
1,4-Dioxane	2.21	79.2	279.9	+25.2	321.4	+87.8	0.213	0.113
Benzene	2.28	76.5	277.2	+22.5	318.7	+85.1	0.217	
Di-*n*-butyl Ether	3.08	53.9	254.6	−0.1	296.1	+62.5	0.196	
Tetrahydrofuran	7.58	15.6	216.3	−38.4	257.8	+24.2	0.141	0.104
Dichloromethane	8.93	11.6	212.3	−42.4	253.8	+20.2	0.119	0.078
Propionitrile	27.2	−3.3	197.4	−57.3	238.9	+5.3		
Acetonitrile	37.5	−5.3	195.4	−59.3	236.9	+3.3	0.102	0.074

[a)] Calculated according to eq. (3) with a = 7 Å (see ref.[15] and references therein). — [b)] Calculated according to eq. (2) with $E^{\mathrm{Red}}_{1/2}$ (**1**) = −1.66 V vs. Ag/AgNO$_3$ and $\Delta E_{\mathrm{excit}}$ = 254.7 kJ/mol (singlet energy of **1**, taken from fluorescence at 470 nm). For $E^{\mathrm{Ox}}_{1/2}$ (**2d**) see Table 1. — [c)] Calculated according to eq. (2) with $\Delta E_{\mathrm{excit}}$ = 233.6 kJ/mol (ref.[34]). For $E^{\mathrm{Ox}}_{1/2}$ (**3b**) see Table 1. See also note b).

(3.3 kJ/mol) indicates that SSIP formation should be possible. Therefore even in this system Φ_P shows the normal behaviour, but the absolute decrease is smaller (see above).

2. Discussion

2.1. Exciplex Formation and Electron Transfer

The fluorescence and phosphorescence of biacetyl were quenched by the alkenes **2**–**6** with various efficiences. Although electron transfer is not the primary step (chapter 1.2) the result shown in Table 1 and Figure 1 reveal a strong dependence on the oxidation potential of the quencher and, as a consequence, on ΔG_2 of electron transfer [equation (2)]. Figure 4 shows the correlation between log k_q and ΔG_2 of SSIP formation in acetonitrile.

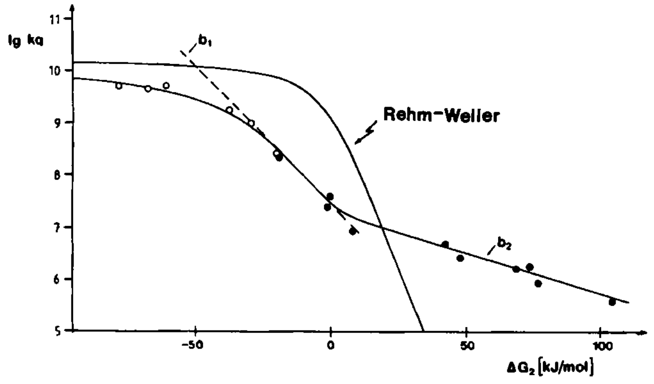


Figure 4. Semilogarithmic plot of the rate constants for luminescence quenching of biacetyl (**1**) in acetonitrile as a function of the free enthalpy change for complete electron transfer, calculated by means of equation (2) (o/● quenching of fluorescence/phosphorescence). Slope b_1 = 0.060 mol/kJ, b_2 = 0.018 mol/kJ

The S shape of this correlation completely differs from the Rehm-Weller curve which is expected for a direct electron transfer. Three different regions may be distinguished:

(i) For $\Delta G_2 > 0$ the slope (s = 0.0178 mol/kJ) is about 10% of that expected from the Rehm-Weller correlation and is in accordance with that reported by Jones for phosphorescence quenching of **1** by various olefins in benzene[6].

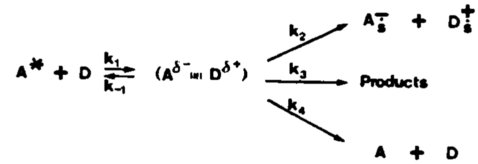
(ii) For $\Delta G_2 < -30$ kJ/mol the k_q values are smaller than predicted by Rehm and Weller for an exergonic complete electron transfer process.

(iii) For $0 > \Delta G_2 > -30$ kJ/mol the slope is -0.06 mol/kJ.

In order to rationalize these effects we have extended the "exciplex mechanism" to ionic photodissociation (Scheme 6).

The reversibly formed exciplex may be deactivated via three pathways: by electron transfer with formation of solvated radical ions (ionic photodissociation k_2), by product formation (k_3), and by decay into the ground state (k_4). According to Scheme 6 the rate constant for quenching the excited acceptor (k_q) and the free enthalpy of exciplex formation are given by equations (4) and (5):

Scheme 6. Extended exciplex mechanism to ionic photodissociation



$$k_q = \frac{k_1(k_2+k_3+k_4)}{k_{-1}+k_2+k_3+k_4} \qquad (4)$$

$$K_{ex} = \frac{k_1}{k_{-1}} = \exp\left(-\frac{\Delta G_{ex}}{RT}\right). \qquad (5)$$

With equation (6)[25,39] ΔG_{ex} can be calculated from the easily accessible free enthalpies of electron transfer ΔG_2 [see eq. (2)]

$$\Delta G_{ex} = b^2\Delta G_2 = \frac{s}{0.178\,\mathrm{mol/kJ}}\Delta G_2 \qquad (6)$$

where b^2 is the fraction of the electron transferred from donor to acceptor molecule. b^2 can be obtained from the slope s of log k_q vs. ΔG_2[25] (Figure 4) with 0.178 mol/kJ as the maximal slope, which is expected for a complete electron transfer in the luminescence quenching process[14a].

The free enthalpy of activation $\Delta G_1^{\ddagger}$ may be calculated similarly to $\Delta G_2^{\ddagger}$ [see below, eq. (9)] according to Rehm and Weller[14a]:

$$\Delta G_1^{\ddagger} = \frac{\Delta G_{ex}}{2} + \left[\left(\frac{\Delta G_{ex}}{2}\right)^2 + (\Delta G_1^{\ddagger}(0))^2\right]^{0.5} \qquad (7)$$

In order to obtain a correlation between log k_q and ΔG_2 we further assume:

(i) The rate constants k_3 and k_4 do not depend on ΔG_2[40]. k_2 is calculated according to Rehm and Weller[14a] by means of eqs. (8) and (9)

$$k_2 = k_2^0\exp\left(-\frac{\Delta G_2^{\ddagger}}{RT}\right) \qquad (8)$$

$$\Delta G_2^{\ddagger} = \frac{\Delta G_2}{2} + \left[\left(\frac{\Delta G_2}{2}\right)^2 + (\Delta G_2^{\ddagger}(0))^2\right]^{0.5} \qquad (9)$$

(ii) ΔG_{ex} is calculated with $s = -0.0178$ mol/kJ ($b^2 = 0.1$, i.e. 10% of the "Rehm-Weller slope") as we have found for $\Delta G_2 > 0$ (see Figure 4).

(iii) The free enthalpy of activation for exciplex formation is $\Delta G_1^{\ddagger}$ (0) = 5 kJ/mol, i.e. smaller than $\Delta G_2^{\ddagger}$ (0)[14a]. This corresponds to a small reorganization energy according to the Marcus theory. Similar effects have been observed by Loutfy[39].

(iv) $\Delta G_2^{\ddagger}$ (0) = 16.7 kJ/mol; this value is larger than the lower limit calculated by Rehm and Weller (10 kJ/mol), but still smaller than the reorganization energies found for other electron transfer reactions[41,42].

(v) $k_{10} = 2 \cdot 10^{10}\ \mathrm{M^{-1}\,s^{-1}}$ (diffusion-controlled limit[14a]). With $k_2^0 = 10^{10}\ \mathrm{s^{-1}}$ and $k_3 + k_4 = 2 \cdot 10^7\ \mathrm{s^{-1}}$ the calculated curve and the experimental data for the dependence of log k_q on ΔG_2 are in good agreement (Figure 4) supporting our proposed mechanism (Scheme 6). For further details of this calculation see elsewhere[43].

Table 4. Rate constants of biacetyl/olefin systems and calculated exciplex lifetimes according to Scheme 6

ΔG_{et} [kJ/mol]	$10^{-8}k_1$ [M^{-1} s^{-1}]	$10^{-8}k_{-1}$ [s^{-1}]	$10^{-7}k_3$ [s^{-1}]	$10^{-7}k_2$ [s^{-1}]	τ_{ex}[a)] [ns]
+41.9	9.1	51	2	0.01	0.20
0	25	25	2	1.0	0.39
−62.8	64	4.9	2	180	0.44
−83.7	76	2.4	2	270	0.34

[a)] $\tau_{ex} = (k_{-1} + k_2 + k_3 + k_4)^{-1}$.

Table 4 shows some rate constants of the biacetyl/olefin systems. In the range $-20 > \Delta G_2 > -60$ kJ/mol k_2 is $(0.1-2) \cdot 10^9$ s^{-1} in acetonitrile at 25°C, i.e. well below the diffusion-controlled limit. These values are in good agreement with Weller's $k_{diss}^{ex} = 4.9 \cdot 10^8$ s^{-1} for the pyrene/*N,N*-dimethylaniline system[14d)]. The calculated exciplex lifetimes τ_{ex} are nearly constant (0.2−0.5 ns) over the whole ΔG_2 range. In our model a decrease in k_{-1} is compensated by an increase of k_2 (ionic photodissociation).

Moreover, our results somewhat differ from Peter's investigations of the picosecond dynamics of the Paterno-Büchi reaction[28)]. According to this author the benzophenone triplet is quenched by various olefins with half-lifes of formation of transients in the ps time region. These transients are assigned to 1,4-biradicals which are in equilibrium with contact ion pairs (CIP) and which either form products or dissociate into solvated radical ions in subsequent processes. On the other hand the lifetimes of intermediates in biacetyl systems do not vary significantly with the quencher (τ_{ex}). A σ-bond formation (1,4-biradical) should be more sensitive to structural variations of the quencher than π-bonded complex formation involving charge-transfer interaction. Exciplexes have also been proposed in other acceptor/donor systems even in negative ΔG_2 regions[41,44−48)]. A clear differentiation between an exciplex with a certain degree of CT character and a contact ion pair is not yet possible even for systems of exergonic electron transfer. Further evidence for the competition between ionic photodissociation and product formation was obtained from an analysis of the solvent-dependent product formation according to Mataga and Masuhara and is described elsewhere[9c,43)].

2.2. Photoinduced Charge Transfer and Product Formation

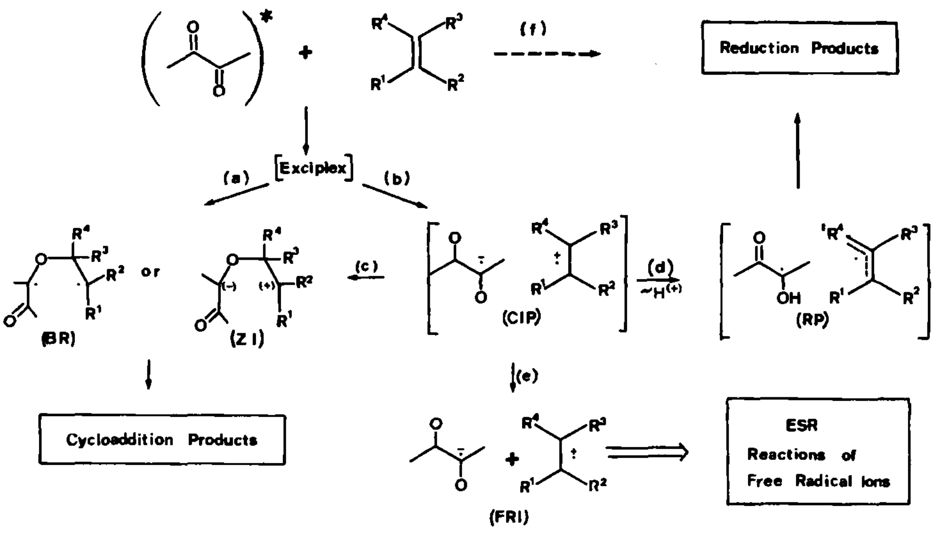
From our results we propose a mechanism as shown in Schemes 7 and 8 which are only more detailed representations of Scheme 6. Here a central point is the photoinduced charge separation. If electron transfer becomes exergonic in polar solvents ionic photodissociation competes with product formation. The solvated radical ions (SSIP and/or FRI) can be detected by ESR or can be scavanged, e.g. by nucleophiles in case of the radical cations.

The formation of cycloaddition and reduction products require some detailed discussion.

Reduction: H-abstraction is the key-step of the formation of reduction products. We assume a two-step mechanism for this process as shown in Scheme 7, i.e. via electron and proton transfer (path b and d), since: (i) Reduction increases from 47 to 90% by increasing exergonity of electron transfer; the difference of 0.06 V of the oxidation potentials of **2c** and **2d** reflects a difference of 5.8 kJ/mol in ΔG_2. (ii) For **1** + **2c** the reduction decreases more than cycloaddition when using polar rather than nonpolar solvents. That means that H-abstraction is more sensitive to the competition with ionic photodissociation indicating polar species as intermediates at least in photoreactions with strong donors like **2c** and **2d**. Note that Arimitsu reported about H-abstraction via excited EDA complexes in benzophenone/amine systems[49)].

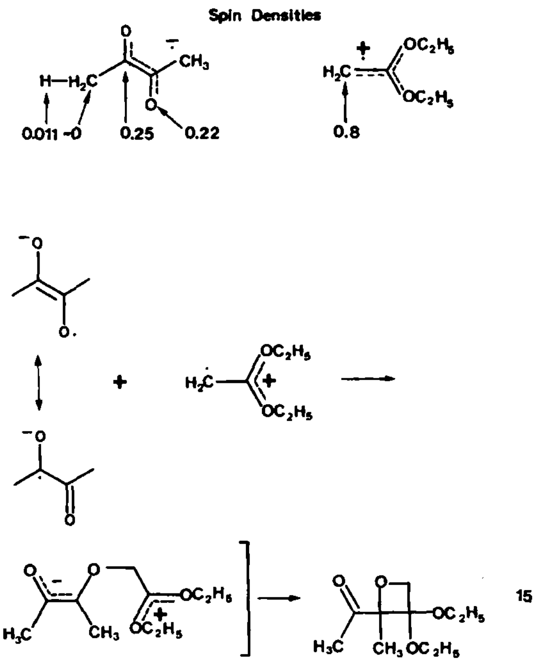
One step H-abstraction (path f) should occur in systems of weak CT character as shown for other ketone/olefin systems[43,50)]. The photoreaction of biacetyl with tetramethylethene (**3e**) which has been studied by Turro[5)] may take an intermediate position between these two extreme mechamisms.

Scheme 7. Exciplex mechanism of photoreactions of biacetyl (**1**) with olefins extended to electron transfer



Cycloaddition: A differentiation between path a and c may be possible only for extreme cases. For **1** + **3b** a reaction sequence b,c may be reasonable: Since ionic photodissociation has been proven (see chapter 1.3) and due to the small ΔG_2 we assume an electron transfer in the photoreaction of **1** with **3b** with formation of a contact ion pair (CIP) or at least of an exciplex of extreme CT character. Evidence for a mechanism involving first e-transfer and secondly σ-bond formation to a zwitterion (ZI) is given by the most important VB structures of $\mathbf{1}^{\overline{\cdot}}$ and $\mathbf{3b}^{\overset{+}{\cdot}}$ which are obtained from ESR measurements[51,52] (Scheme 8): The 1,1-diethoxyethene radical cation with approx. 80% of spin density at the 2-position may couple with the ketyl-type structured semidione radical anion via the radical centers at oxygen and carbon, respectively, yielding the most efficiently stabilized zwitterion. Since the thermal cycloaddition exclusively proceeds aldol-like[19] (Scheme 4) the photochemically induced electron transfer causes an inversion ("Umpolung") of the reactivity of biacetyl[9b].

Scheme 8. Regioselective oxetane formation between biacetyl (**1**) and 1,1-diethoxyethene (**3b**)



Incomplete e-transfer yields 1,4-biradicals as intermediates which give regioisomeric oxetanes in case of unsymmetrical olefins depending on the stabilization effects of the substituents.

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Experimental

Materials: The commercially available olefins **3d**, **3e**, **4a**, **4b**, **5**, and **6** were purified by distillation under argon. Biacetyl (**1**) was distilled under reduced pressure at room temperature and was condensed using a CO_2/acetone cooling mixture directly before use[9c,20]. The other olefins were prepared according to literature: **2a**[53], **2b**[53], **2c**–**f**[16], **3a**[54,55], **3b**[56], **3c**[57]. Spectrophotometric-grade solvents (from Fluka or Merck, respectively) were used for quantitative measurements (for special procedures of purification see below). For preparative procedures the solvents were purified by standard methods. Especially peroxides were removed from ethers and dichloromethane was distilled over potassium carbonate.

Chromatographic Equipment: Gaschromatographic analyses: Carlo Erba Fractovap 2101, OV 17, OV 101 and NPGS glass columns, 5–10% on Chromosorb WAW DMCS 80/100 mesh. – Semipreparative separations of product mixtures: either GC (Philips Unicam GCV, 10% OV 17 on Chromosorb WAW DMCS 80/100 mesh) or HPLC (Gilson-303 Chromatograph, Merck Licrosorb Si 60). – Analytical HPLC: Perkin Elmer Ser. 3-LC-65 T model with the same column type.

Instrumental Analysis: IR spectra: Perkin-Elmer 377 spectrometer. – ^1H- and ^{13}C-NMR spectra: Varian EM 390 (90 MHz), T 60 (60 MHz), and CFT 20 (20 MHz) spectrometer, respectively. – GC-MS: Varian 3700 (15 m, OV 101 capillary), Varian MAT 212, 70 eV. – Absorption spectra: Perkin Elmer 320 spectrometer. – For emission spectra (Stern-Volmer analysis), fluorescence and phosphorescence lifetime measurements see ref.[20]. – Cyclic Voltametry: Voltage Scan Generator (Mod. VSG 72) and Labor-Potentiostat LB 81 H (both from G. Blank Elektronik).

Analytical Irradiations: Irradiations for analytical purposes were performed in a "merry-go-round" apparatus (from H. Mangels, Bornheim-Roisdorf) fitted with an immersion well (pyrex). The following light filter solution[58] was used for n,π* excitation of biacetyl: A saturated solution of $CuSO_4$ and $NaNO_2$ in conc. aqueous NH_3 was diluted 1:5 with conc. aqueous NH_3, transmission at d = 1 cm: 400–480 nm.

1) *Preparative Photoreactions and Product Isolation:* The preparative irradiations were carried out in a photoreactor which was fitted with an immersion well (pyrex glass) and a high pressure mercury lamp HPK 125 W (Philips). In order to prevent acid-catalyzed side reactions all glass apparatures were immersed over night in an aqueous sodium hydroxide solution. A solution of $CuSO_4$ and $NaNO_2$ in aqueous NH_3 was used as light filter (see analytical irradiations). A 1:1 mixture of biacetyl (2,3-butanedione) (**1**) and the corresponding olefin (**2a**–**d**: 0.1 M; **3b**: 0.01–0.1 M) in benzene or cyclohexane (350 ml) was irradiated under nitrogen. The reaction mixture was checked by analytical GC. After ca. 20–30 h **1** was completely consumed (decolorization of the yellow solution) and the mixture was worked up: After removal of the solvent by distillation at room temp. the product mixture was generally first filtered over silica gel (Woelm, 32–100 mesh) in order to remove polymeric materials and then separated by semipreparative HPLC. Mixtures of ethyl acetate (10–35%) in n-hexane (or n-heptane) were used as eluents. The oxetanes **7b** and **8b** (from **1** + **2b**) were separated by semipreparative GC. Only **15** (from **1** + **3b**) could be isolated by distillation.

2) *Products from* **1** + **2a**: Product ratio **7a**:**8a**:**9** = 1.2:1.0:1.1 in benzene. After distillation at 50–60°C/0.4 Torr (Kugelrohr) the mixture (60% yield) was either separated by semipreparative GC or by HPLC (ethyl acetate/n-hexane 35:65 as eluent). Both methods yielded the same results.

exo-7-Acetyl-endo-7-methyl-2,4,6-trioxabicyclo[3.2.0]heptane (**7a**): Colourless oil. – IR ($CDCl_3$): 1720 cm^{-1} (C=O). – ^1H NMR (90 MHz, C_6D_6): δ = 1.08 (s, 3H, CH_3), 1.90 (s, 3H, CH_3CO), 4.63 and 5.52 (AB, *J* = 2.7 Hz, 2H, CHO and OCHO), 5.03 and 5.10 (2 × s, 2H, O_2CH_2), a NOE (8%) between *endo*-7-CH_3 and O_2CH (at δ = 5.03) further confirms the *exo*-configuration of **7a**. – ^1H NMR (90 MHz, CCl_4): δ = 1.28 (s, 3H, CH_3), 2.23 (s, 3H, CH_3CO), 4.75 and 5.90 (AB, *J* = 2.7 Hz, 2H, CHO and OCHO), 5.23 and 5.37 (2 × s, 2H, O_2CH_2). – ^{13}C NMR (20 MHz, C_6D_6): δ = 16.84 (CH_3), 24.24 (CH_3CO); 81.48 (CHO), 96.93 (O_2CH_2), 102.38 (OCHO). – MS: *m/z* (%) = 158 (0.3, M^+), 157 (3.2, M^+ – 1), 127 (3.0), 116 (8.1), 115 (16.1, M^+ – CH_3CO), 99 (2.8), 87 (5.5), 86 (3.5, $\mathbf{1}^+$), 85 (18.2, $\mathbf{1}^+$ – 1), 73 (3.1), 72 (3.3, $\mathbf{2a}^+$), 71 (6.5), 43 (100, CH_3CO^+).

$C_7H_{10}O_4$ (158.2) Calcd. C 53.16 H 6.37
Found C 52.92 H 6.20

endo-7-Acetyl-exo-7-methyl-2,4,6-trioxabicyclo[3.2.0]heptane (**8a**): Colourless oil. – IR ($CDCl_3$): 1720 cm^{-1} (C=O). – ^1H NMR (90 MHz, C_6D_6): δ = 1.02 (s, 3H, CH_3), 1.85 (s, 3H, CH_3CO), 4.18 and 5.52 (AB, *J* = 2.7 Hz, 2H, CHO and OCHO), 4.87 and 4.97 (2 × s, 2H, O_2CH_2), a NOE between *exo*-7-CH_3 and CHO (16%) and OCHO (8%), respectively, but no NOE between *exo*-7-CH_3 and O_2CH_2 confirm the *endo*-configuration. – ^1H NMR (90 MHz, CCl_4): δ = 1.50 (s, 3H, CH_3), 2.13 (s, 3H, CH_3CO), 4.73 and 5.90 (AB, *J* = 2.7 Hz, 2H, CHO and OCHO), 4.92 and 5.25 (2 × s, 2H, O_2CH_2). – ^{13}C NMR (20 MHz, C_6D_6): δ = 22.46 and 24.49 (CH_3), 83.55 (CHO), 96.14 (O_2CH_2), 100.98 (OCHO). – MS: *m/z* (%) = 158 (0.3, M^+), 157 (4.1, M^+ – 1), 127 (3.7), 116 (9.4), 115 (18.9, M^+ – CH_3CO), 99 (3.1), 87 (5.6), 86 (3.9, $\mathbf{1}^+$), 85 (20.9, $\mathbf{1}^+$ – 1), 73 (3.5), 72 (3.7, $\mathbf{2a}^+$), 71 (7.2), 43 (100, CH_3CO^+).

$C_7H_{10}O_4$ (158.2) Calcd. C 53.16 H 6.37
Found C 52.94 H 6.14

3,4-Dimethyl-2,5,7,9-tetraoxabicyclo[4.3.0]non-3-ene (**9**): Colourless oil. – ^1H NMR (90 MHz, C_6D_6): δ = 1.80 (s, 6H, CH_3), 4.23 (s, 2H, OCHO), 4.76 (s, 2H, O_2CH_2). – ^1H NMR (90 MHz, CCl_4): δ = 2.23 (s, 6H, CH_3), 4.40 (s, 2H, OCHO), 5.02 (s, 2H, O_2CH_2). – ^{13}C NMR (20 MHz, C_6D_6): δ = 25.81 (CH_3), 81.57 (OCHO), 96.53 (O_2CH_2). – MS: *m/z* (%) = 158 (0.5, M^+), 157 (4.6, M^+ – 1), 127 (8.7), 116 (1.0), 115 (7.1), 99 (37.1), 86 (2.4, $\mathbf{1}^+$), 85 (10.9, $\mathbf{1}^+$ – 1), 73 (2.0), 72 (1.6, $\mathbf{2a}^+$), 71 (8.9), 43 (100, CH_3CO^+).

$C_7H_{10}O_4$ (158.2) Calcd. C 53.16 H 6.37
Found C 53.29 H 6.54

3) *Products from* **1** + **2b**: Product ratio **7b**:**8b** = 0.6/0.5/0.3 in cyclohexane and benzene/tetrahydrofuran/acetonitrile. The products from the photoreaction in benzene were first distilled at 55°C/0.5 Torr to give a slightly yellowish oil (55% yield) which was then separated into the components by GC.

exo-7-Acetyl-3,3,endo-7-trimethyl-2,4,6-trioxabicyclo[3.2.0]heptane (**7b**): Colourless oil. – IR (neat): 1710 cm^{-1} (C=O). – ^1H NMR (60 MHz, $CDCl_3$): δ = 1.40, 1.52, and 1.73 (3 × s, 3 × 3H, CH_3), 2.30 (s, 3H, CH_3CO), 4.95 and 5.97 (AB, *J* = 3 Hz, 2H, CHO and OCHO).

$C_9H_{14}O_4$ (186.2) Calcd. C 58.05 H 7.58
Found C 58.12 H 7.69 (**7b**/**8b** mixture)

endo-7-Acetyl-3,3,exo-7-trimethyl-2,4,6-trioxabicyclo[3.2.0]heptane (**8b**): Colourless oil. – IR (neat): 1710 cm^{-1} (C=O). – ^1H NMR (60 MHz, $CDCl_3$): δ = 1.36, 1.40, and 1.56 (3 × s, 3 × 3H, CH_3), 2.20 (s, 3H, CH_3CO), 4.90 and 5.90 (AB, *J* = 3 Hz, 2H, CHO and OCHO).

$C_9H_{14}O_4$ (186.2) Calcd. C 58.05 H 7.58
Found C 57.82 H 7.72

Upon reketalisation with acetone in the presence of *p*-toluenesulfonic acid in dichloromethane the product mixture from **1** + **2b** yielded the bisketal **14b**, which was purified by semipreparative GC.

2,4,4,6,10,10-Hexamethyl-3,5,7,9,11-pentaoxatricyclo[6.3.0.0^{2,6}]undecane (**14b**): ^1H NMR (60 MHz, C_6D_6): δ = 1.14 (s, 3H, CH_3), 1.33 (br s, 6H, CH_3), 1.43 (br s, 6H, CH_3), 1.55 (s, 3H, CH_3), 4.30 and 5.77 (AB, *J* = 4 Hz, 2H, CHO and OCHO, respectively).

$C_{12}H_{20}O_5$ (244.3) Calcd. C 59.00 H 8.25
Found C 58.87 H 8.13

4) *Products from* **1** + **2c**: Product ratio **7c**:**8c**:**10a**:**11a**:**12a** = 21:19:25:22:14 in benzene, yield 70% according to NMR analysis. Since the product mixture partly decomposed upon distillation the products were isolated by HPLC (ethyl acetate/*n*-heptane 10:90 as eluent). Besides these products ca. 10% of 3,4-dihydroxy-3,4-dimethyl-2,5-hexanedione (pinakol of **1**) could be isolated.

The structural assignment of **7c** and **8c** was carried out basing on the following arguments: The ratio of *exo*- and *endo*-oxetane depends on the solvent polarity, i.e. generally the *endo*-isomer is favoured in polar solvents (see e.g. **7b** and **8b**). In this case **7c**:**8c** = 1.1/0.6 in benzene/acetonitrile.

exo-7-Acetyl-1,5,endo-7-trimethyl-2,4,6-trioxabicyclo[3.2.0]heptane (**7c**): Colourless oil. – IR (neat): 1720 cm^{-1} (C=O). – ^1H NMR (90 MHz, C_6D_6): δ = 1.04 (s, 6H, CH_3), 1.54 (s, 3H, CH_3), 1.88 (s, 3H, CH_3CO), 4.93 and 4.98 (2 × s, 2H, O_2CH_2).

endo-7-Acetyl-1,5,exo-7-trimethyl-2,4,6-trioxabicyclo[3.2.0]heptane (**8c**): Colourless oil. – ^1H NMR (90 MHz, C_6D_6): δ = 1.07, 1.24, and 1.30 (3 × s, 9H, CH_3), 1.96 (s, 3H, CH_3), 4.75 and 5.05 (2 × s, 2H, O_2CH_2).

$C_9H_{14}O_4$ (186.2) Calcd. C 58.05 H 7.58
Found C 58.29 H 7.77

3-Hydroxy-3-[(5-methyl-1,3-dioxol-4-yl)methyl]-2-butanone (**10a**): Oil. – IR (neat): 3460 cm^{-1} (OH), 1720 (C=O). – ^1H NMR (60 MHz, C_6D_6): δ = 1.22 (s, 3H, CH_3), 1.69 (s, 3H, allyl-CH_3), 2.03 (s, 3H, CH_3CO), 2.41 (s, 2H, allyl-CH_2), 4.06 (br s, 1H, OH), 5.17 and 5.28 (2 × d, *J* = 2 Hz, 2H, O_2CH_2).

$C_9H_{14}O_4$ (186.2) Calcd. C 58.05 H 7.58
Found C 58.22 H 7.80

3-Hydroxy-3-(4-methyl-5-methylene-1,3-dioxol-4-yl)-2-butanone, Isomer **11a** (Main Isomer): Oil. – IR (neat): 3450 cm^{-1} (OH), 1710 (C=O), 1680 (C=C). – ^1H NMR (60 MHz, C_6D_6): δ = 1.16 and 1.27 (2 × s, 6H, CH_3), 2.12 (s, 3H, CH_3CO), 4.33 (br s, 1H, OH), 4.46 and 4.58 (2 × d, *J* = 2 Hz, 2H, =CH_2), 4.79 and 4.96 (2 × s, 2H, O_2CH_2).

$C_9H_{14}O_4$ (186.2) Calcd. C 58.05 H 7.58
Found C 58.18 H 7.72

Isomer **12a** (Minor Isomer): Oil. – IR (neat): 3450 cm^{-1} (OH), 1710 (C=O), 1680 (C=C). – ^1H NMR (60 MHz, C_6D_6): δ = 1.29 and 1.41 (2 × s, 6H, CH_3), 2.07 (s, 3H, CH_3CO), 4.11 and 4.38 (2 × d, *J* = 2 Hz, 2H, =CH_2), 4.24 (br s, 1H, OH), 4.77 and 4.93 (2 × s, 2H, O_2CH_2).

3,4-Dihydroxy-3,4-dimethyl-2,5-hexanedione (Pinakol of **1**): This side product was isolated by HPLC as the component with the shortest retention time. It probably was formed during the work-up procedure by hydrolysis from the oxetane **7c** and **8c** or from **11a** and **12a**, since the product mixture did not show any trace of the pinakol. – IR (C_6D_6): 3450 cm^{-1} (OH), 1700 (C=O). – ^1H NMR (60 MHz, C_6D_6): δ = 1.06 and 1.22 (2 × s, 6H, CH_3), 2.04 and 2.13 (2 × s, 6H, CH_3CO), 4.40 (br s, 2H, OH).

5) *Products from* **1** + **2d**: Product ratio **10b**:**11b**:**12b** = 7:2:1 in benzene, yield 65% according to NMR analysis. Two additional products were formed in ca. 5%. No pinakol from **1** could be detected during the photoreaction. The products were isolated by HPLC with ethyl acetate/*n*-hexane (10:90) as eluent.

3-Hydroxy-3-[(2,2,5-trimethyl-1,3-dioxol-4-yl)methyl]-2-butan one (**10b**): Oil. – IR (neat): 3480 cm^{-1} (OH), 1715 (C=O). – ^1H NMR (60 MHz, CCl_4): δ = 1.28, 1.35, and 1.42 (3 × s, 9H, CH_3), 1.72 (s, 3H, allyl-CH_3), 2.18 (s, 3H, CH_3CO), 2.42 (s, 2H, allyl-CH_2), 3.73 (br s, 1H, OH).

$C_{11}H_{18}O_4$ (214.3) Calcd. C 61.66 H 8.47
Found C 61.42 H 8.28

3-Hydroxy-3-(2,2,4-trimethyl-5-methylene-1,3-dioxol-4-yl)-2-butanone, Isomer **11b** (Main Isomer): Oil. – ^1H NMR (60 MHz, CCl_4): δ = 1.28, 1.35, 1.43, and 1.53 (4 × s, 12H, CH_3), 2.30 (s, 3H, CH_3CO), 4.03 (br s, 1H, OH), 4.23 and 4.37 (2 × d, *J* = 2 Hz, 2H, $=CH_2$).

Isomer **12b** (Minor Isomer): Oil. – ^1H NMR (60 MHz, CCl_4): δ = 1.35 and 1.42 (2 × s, 6H, CH_3), 1.53 (br s, 6H, CH_3), 2.27 (s, 3H, CH_3CO), 3.27 (br s, 1H, OH), 4.02 and 4.33 (2 × d, *J* = 2 Hz, 2H, $=CH_2$). – The pre-purified product mixture showed the following microanalytical data.

$C_{11}H_{18}O_4$ (214.3) Calcd. C 61.66 H 8.47
Found C 61.50 H 8.35

Upon reketalization with acetone in the presence of *p*-toluenesulfonic acid in dichloromethane the product mixture from **1** + **2d** yielded two ketals in 7:3 ratio which were separated by means of semipreparative GC.

7-Acetyl-1,3,3,7-tetramethyl-2,4,8-trioxabicyclo[3.3.0]octane (**13**) (Main Component): ^1H NMR (90 MHz, C_6D_6): δ = 1.14 (s, 6H, CH_3), 1.30 and 1.48 (2 × s, 6H, CH_3), 2.29 (s, 3H, CH_3CO), 2.13 (d, *J* = 9.5 Hz, 1H, CH_2), 2.94 (d, *J* = 14.0 Hz, 1H, CH_2), 4.18 (d, *J* = 5.4 Hz, 1H, CHO). – ^{13}C NMR (20 MHz, C_6D_6): δ = 25.01, 25.47, 25.49, 26.22 (CH_3), 40.81 (CH_2), 84.35 (CHO), 90.17 (tert. CO), 110.20 and 114.42 (OCO), 210.27 (C=O).

$C_{11}H_{18}O_4$ (214.3) Calcd. C 61.66 H 8.47
Found C 61.38 H 8.20

1,2,4,4,6,8,10,10-Octamethyl-3,5,7,9,11-pentaoxatricyclo[6.3.0.0^{2,6}]-undecane (**14a**): ^1H NMR (90 MHz, C_6D_6): δ = 1.27, 1.28, 1.33, 1.41, 1.42, and 1.60 (6 × s, same intensity, CH_3). – ^{13}C NMR (20 MHz, C_6D_6): δ = 17.35, 23.34, 28.35, and 29.83 (CH_3), 90.93 (tert. CO), 109.31 and 113.85 (OCO).

$C_{14}H_{24}O_5$ (272.3) Calcd. C 61.74 H 8.88
Found C 61.38 H 8.59

6) *Products from* **1** + **3b**: Distillation of the oil-residue after work-up (see above) gave:

2-Acetyl-3,3-diethoxy-2-methyloxetane (**15**): 69% yield; b.p. 39–40°C/0.1 Torr. – IR (neat): 1717 cm^{-1} (C=O). – ^1H NMR (60 MHz, CCl_4): δ = 1.19 and 1.17 (2 × t, *J* = 7 Hz, 6H, OEt), 1.40 (s, 3H, CH_3), 2.21 (s, 3H, CH_3CO), 3.41 and 3.45 (2 × q, *J* = 7 Hz, 4H, OEt), 4.40 (s, 2H, CH_2O). – ^{13}C NMR (20 MHz, C_6D_6): δ = 15.06 and 15.56 (CH_3, of OEt), 18.80 (CH_3), 26.39 (CH_3CO), 58.12 and 58.61 (CH_2 of OEt), 76.10 (CH_2O), 97.88 (C-2), 102.17 (C-3), 208.68 (C=O).

$C_{10}H_{18}O_4$ (202.3) Calcd. C 59.39 H 8.97
Found C 59.52 H 9.13

The same reaction in acetonitrile yielded besides **15** two compounds. One could be isolated by means of HPLC using with ethyl acetate/hexane (5:95) as eluent and was identified as:

Ethyl 3-Ethoxycrotonate (**18**): IR (neat): 1710 cm^{-1} (C=O), 1635 (C=C). – ^1H NMR (90 MHz, $CDCl_3$): δ = 1.26 and 1.33 (2 × t, *J* = 7 Hz, 6H, CH_3), 2.30 (s, 3H, CH_3), 3.81 and 4.12 (2 × q, *J* = 7 Hz, 4H, CH_2), 5.00 (s, 1H, =CH).

The product mixture also showed the typical spectroscopic data of *ethyl 3,3-diethoxybutanoate* (**17**): IR (neat): 1737 cm^{-1} (C=O). – ^1H NMR: additional signals at 3.5 (OEt), 2.6 (CH_2CO), and 1.0–1.5 (OEt). The spectroscopic data are identical with those of an authentic mixture of **17** and **18** which had been prepared according to ref.[32,33].

7) *Luminescence Quenching:* The luminescence spectra were recorded at 20°C. Samples containing biacetyl (**1**) and an olefin as quencher were deoxygenated by bubbling argon through the solutions in triangular cuvettes. The Stern-Volumer relationship have been measured over a concentration range with a factor of at least 10/50 for electron-rich/normal and electron-deficient olefins. No deviations other than statistical ones have been observed. A more detailed description for the luminescence quenching of **1** and the fluorescence and phosphorescence lifetime measurements as well is reported elsewhere[20].

8) *Sensitization Experiments with Benzophenone:* Benzophenone (BP) was chosen as sensitizer for biacetyl (**1**) for following reasons:

(i) The intersystem crossing (isc) of BP is more efficient than of **1**, $k_{isc} \approx 10^{11}\ s^{-1}$, $\Phi_{isc} \approx 1$, $\Phi_F < 10^{-4}$[59].

(ii) The energy transfer (ET) from BP to **1** is exothermic, E_T (BP) = 288 kJ/mol (≙ 415 nm)[58] and E_T (**1**) = 233.6 kJ/mol[34], and therefore k_{ET} ($^3BP^*$/**1**) should be diffusion-controlled.

(iii) The nπ* excitation of BP (λ = 320–380 nm) conveniently fits into the gap of nπ* and ππ* absorption band of **1**.

(iv) BP shows phosphorescence at room temperature, i.e. Stern-Volmer quenching experiments are feasable under these conditions.

A solution of BP (1 mol/l) and **1** (0.2 mol/l) in benzene was investigated with respect to absorption and emission properties. At λ = 366 nm almost all light is absorbed from BP: With ε^{366} (BP) = 67 l mol^{-1} $cm^{-1}$and ε^{366} (**1**) = 3.6 l mol^{-1} cm^{-1} η^{abs} (BP) = 0.989. The rate constant of phosphorescence quenching of BP by **2d** has been determined by Stern-Volmer analysis: k_q (BP/**1**) = 2.44×10^9 l mol^{-1} s^{-1} with $\tau(^3BP^*)$ = 2.2 μs[60]. The rate constant of energy transfer from $^3BP^*$ to **1** in benzene has also been determined by quenching of the BP-phosphorescence by **1**: k_{ET} ($^3BP^*$)/**1**) = 1.13×10^{10} l mol^{-1} s^{-1}, i.e. diffusion-controlled[61]. Using these data the appropriate concentration of the olefin is < 0.2 mol/l, i.e. ca. 99% of triplet-BP only react with **1** by energy transfer (for details of the calculation see Leismann[62]).

Two sensitization experiments at λ = 366 nm [DEMA UVW 55 filter, transmission at 366 nm = 54% with BP (1 mol/l) and **1** (0.2 mol/l)] in the presence of the olefin **2a** or **2d** (both 0.01 mol/l) were carried out in benzene solution. For comparison with pure singlet reactions solutions of **1** (0.2 mol/l) and the same olefins (0.2 mol/l) in benzene (almost complete fluorescence quenching of **1**) were irradiated as well. There was no difference in product formation under S_1 and T_1 conditions in both cases according to GC-analysis.

9) *Measuring of Quantum Yields, Electrochemical Redox Potentials, and ESR Spectra:* Values of product quantum yields Φ_P were determined with an irradiation set-up and the potassium ferri oxalate actinometer which has already been described elsewhere[63]. For the solvent dependence of Φ_P a "merry-go-round" apparatus was used. The product formation was measured by GC (internal standard method) at max. 5% conversion.

Half-peak redox potentials were obtained by cyclic voltametry at a platinum electrode and an Ag/0.1 M $AgNO_3$ reference electrode (concentration 10^{-3} M). Tetra-*n*-butylammonium tetrafluoroborate (0.1 M) was used as supporting electrolyte and acetonitrile was dried by filtration over basic Al_2O_3 (activated at 300°C, 0.1 Torr). The scan speed was 100 mV/s; half-peak potentials were taken as the half-wave potentials.

ESR spectra were recorded at the Max-Planck-Institut für Strahlenchemie (Mülheim) under in-situ-photolysis conditions in acetonitrile at 0°C. The experimental set-up has already been described[30].

CAS Registry Numbers

1: 431-03-0 / **1** (pinacol deriv.): 28123-56-0 / **2a**: 288-53-9 / **2b**: 22945-10-4 / **2c**: 85976-13-2 / **2d**: 85976-14-3 / **3b**: 2678-54-8 / **7a**: 105786-16-1 / **7b**: 105786-18-3 / **7c**: 105786-20-7 / **8a**: 105879-65-0 / **8b**: 105978-66-1 / **8c**: 105879-67-2 / **9**: 105786-17-2 / **10a**: 105786-21-8 / **10b**: 89435-01-8 / **11a**: 105786-22-9 / **11b**: 105786-24-1 / **12a**: 105786-23-0 / **12b**: 105786-25-2 / **13**: 105786-26-3 / **14a**: 105817-81-0 / **14b**: 105786-19-4 / **15**: 89435-03-0 / **17**: 60702-49-0 / **18**: 998-91-4

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[1] The two related series "Selectivity and Charge Transfer in Photoreactions of Donor-Acceptor Systems" (A) and "Radical Ions" (B) have now been combined. This paper now counts as part 16 of our new series: "*Radical Ions and Photochemical Charge Transfer Phenomena*". — [1a] Part 12, series A: J. Mattay, *Selectivities in Photoreactions of Arenes to Olefins, J. Photochem.*, in press. — [1b] Part 11, series A: J. Mattay, J. Runsink, R. Hertel, J. Kalbe, I. Schewe, *Stereoselectivities in meta-Photocycloadditions of Phenol Ethers to Olefins, J. Photochem.*, in press. — [1c] Part 3, series B: J. Gersdorf, J. Mattay, H. Görner, *J. Am. Chem. Soc.*, in press.

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