Two-Photon Chemistry in the Laser Jet: Photochemistry of the Diphenylhydroxymethyl Radical

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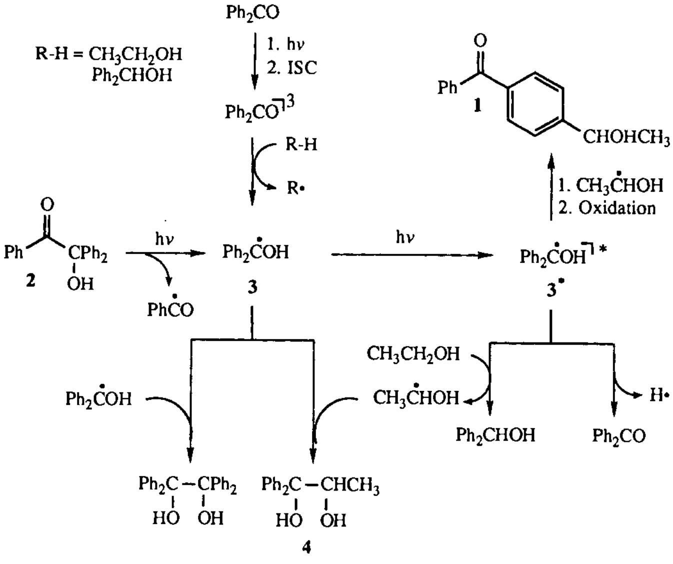
In the laser-jet mode (argon ion laser) the excited hydroxydiphenylmethyl radical ($\mathbf{3}^*$) underwent H expulsion in inert solvents (benzene, acetonitrile) to produce benzophenone (two-photon product), besides dimerization of its ground state **3** to benzpinacol (one-photon product). In ethanol, the laser-jet photolysis of benzophenone afforded as new products (two-photon chemistry) benzhydrol, 4-(1-hydroxyethyl)benzophenone (**1**), together with benzpinacol and 1,1-diphenyl-1,2-propandiol (**4**), which are also observed in low-intensity photolyses (one-photon chemistry). Benzhydrol is formed through H abstraction from the excited radical $\mathbf{3}^*$ and ketone **1** possibly by coupling of an excited radical $\mathbf{3}^*$ at its *para* position (highest spin density) with a transient 1-hydroxyethyl radical. Photolysis of α-phenylbenzoin (**2**) produced benzpinacol, benzophenone, pinacol **4**, benzhydrol, ketone **1**, and the benzoyl-derived products benzil and benzaldehyde. Also benzhydrol was observed as a two-photon product.

The product distribution in the photoreduction of benzophenone in aliphatic alcohols has been found to depend on the light intensity used[1,2]. This suggests that short-lived intermediates suffered photolysis. Indeed, the intermediary hydroxydiphenylmethyl radical[3] (**3**) has a strong absorption at $\lambda = 515$ and below 350 nm[4] and can also be excited by triplet sensitization[5]. The fluorescence emission of the excited radical $\mathbf{3}^*$ has a maximum at $\lambda = 575$ nm[6], and its lifetime has been determined to be 2–4 ns[6–8].



Scheme 1. Photochemical generation and transformations of the hydroxydiphenylmethyl radical (**3**)

Laser excitation in the visible region resulted in irreversible bleaching[7], in which the excited radical $\mathbf{3}^*$ undergoes chemical transformation instead of deactivation to the ground-state radical **3**. This reaction has been shown in nonpolar solvents[7] to be H-atom expulsion and in polar solvents also electron ejection (ca. 20%)[9]. Both intramolecular reactions of the excited radical $\mathbf{3}^*$ yield benzophenone as the final product.

Also intermolecular reactions of the excited radical $\mathbf{3}^*$ have been observed. Quenching experiments with electron acceptors and methyl methacrylate have been carried out[6,8], which confirm that the excited state $\mathbf{3}^*$ is more reactive than its ground state **3**. The most prominent increase in rate occurred in the methyl methacrylate quenching[8], in which an acceleration by a factor of 10^5 was observed.

Despite the abundance of spectroscopic and kinetic data, product studies on the photochemistry of radical **3** are scarce[1,7]. This happenstance derives from the fact that pulsed lasers are optimal tools for time-resolved spectroscopic and kinetic studies but not particularly suited for preparative work. Of advantage for the latter is to use the continuous high-light intensity of the argon ion laser which can be maintained for long periods of time (hours). For this purpose the laser-jet technique was developed as a valuable tool[10], which permits accumulation of enough material for the isolation and characterization or identification of the two-photon products. Presently, we report the results of our investigations on the photolysis of the hydroxydiphenylmethyl radical in the laser-jet mode.

Results

Three different ways were used to generate the hydroxydiphenylmethyl radical (**3**). In the inert solvents benzene and acetonitrile, H abstraction from benzhydrol by triplet benzophenone yielded radical **3** (2 mol) and from ethanol, be-

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Table 1. Product studies of the laser-jet (LJ) and Rayonet photolyses of benzophenone and benzhydrol in inert solvents

Entry	Mode	Solvent	Conc. of Ph_2CHOH [10^2 M]	Starting mixture[a,b] [mmol] Ph_2CHOH	Ph_2CO	Composition [mmol] of the product mixture[a,c] Ph_2CHOH	Ph_2CO	Benzpinacol	Rel. change[d] Ph_2CO (%)
1	Rayonet[e]	C_6H_6	0.97	1.00	1.12	0.43	0.50	0.62	−55
2	LJ[f]	C_6H_6	0.97	1.00	1.12	0.70	1.10	0.09	−2
3	LJ[f]	CH_3CN	1.01	1.00	1.02	0.80	1.04	0.05	+2
4	LJ[f]	CH_3CN	5.08	1.00	0.14	0.85	0.17	0.03	+21

[a] Absolute values, detected by HPLC, error ±5% of stated value. — [b] Normalized to 1 mmol of Ph_2CHOH. — [c] Mass balance better than 90%. — [d] Amount of Ph_2CO converted devided by the initial amount of Ph_2CO used. — [e] Rayonet photoreactor, 350-nm lamps, 1 h irradiation. — [f] Argon-ion laser, continuous operation, 3.6-W all-UV lines (λ = 334, 351, 364 nm), 100-μm capillary, 23 cycles.

sides radical **3** also the 1-hydroxyethyl radical. An alternative access to radical **3** was the Norrish-type I cleavage of ketone **2**.

Upon photolysis of a mixture of benzophenone and benz$_1$hydrol in benzene and acetonitrile, only benzpinacol was formed as a photoproduct. The consumption of benzhydrol and benzophenone varied with the light intensity; the latter constitutes a valuable mechanistic probe for two-photon chemistry. The amounts of all compounds before and after photolyses are listed in Table 1. The absolute values and the relative changes of benzophenone are given instead of conversions (%), because in this reaction benzophenone is starting material and at higher light intensities also product[7].

Upon photolysis at low intensities (Rayonet; Table 1, entry 1) benzhydrol and benzophenone were consumed in nearly equal amounts (0.57 vs. 0.62 mmol). On the other hand, at high intensities of the laser-jet reaction (Table 1, entry 2), benzhydrol was consumed to a large extent (30%), whereas benzophenone decreased only slightly (0.02 mmol, 2% of its initial amount). In this reaction also a small amount of biphenyl was detected.

These differences in the consumption of benzophenone under low- and high-intensity conditions were also found in the more polar solvent acetonitrile. Thus, in the laser-jet mode (Table 1, entry 3) 0.20 mmol of benzhydrol was consumed, but the amount of benzophenone even increased slightly (2%, 0.02 mmol). To test whether benzophenone was indeed a product in the laser-jet photolyses, benzhydrol was used in large excess (Table 1, entry 4). The amount of benzophenone grew significantly (from 0.14 mmol initially to 0.17 mmol finally), i.e. ca. 20% over its initial value, which confirms unequivocally that it is formed in the laser-jet photolyses.

In ethanol, benzophenone was photoreduced to benzpinacol and the unsymmetric pinacol **4**, but also the *para*-coupling product ketone **1** and the H-abstraction product benzhydrol (Table 2) were formed. Thus, upon irradiation in the Rayonet (Table 2, entry 1), both pinacols were the major products (97%), benzhydrol and ketone **1** the minor (together 3%). In the laser-jet mode (Table 2, entry 2), the amount of ketone **1** and benzhydrol grew substantially (together 34%) at the expense of benzpinacol and the unsymmetric pinacol **4** (together 66%). The product distribution varied as well in this case with the laser-light intensity.

The photolysis of ketone **2** in ethanol afforded the same products, but also benzaldehyde and benzil. The amounts of the latter two are not included in Table 2 because, instead of being derived from the hydroxydiphenylmethyl radical (**3**), they are products of the partner benzoyl radical. The Rayonet photolysis (Table 2, entry 3) of ketone **2** yielded mainly benzophenone, benzpinacol, and some unsymmetric pinacol **4** (together 98%) and traces (together ca. 2%) of the ethanol-derived products benzhydrol and ketone **1**. Under laser-jet conditions (Table 2, entry 4), while the amounts of the two solvent-derived products **1** and **4** remained nearly constant, the yield of benzophenone and benzhydrol (together 57%) increased by 17%, predominantly at the expense of benzpinacol, the yield of which dropped from 55% to 37%.

Table 2. Product studies of the laser-jet (LJ) and Rayonet photolyses of benzophenone and benzhydryl phenyl ketone (**2**) in ethanol

Entry	Substrate	Mode	Photolysis time	Conv.[a] (%)	MB[a] (%)	Product distribution[a,b] Benzpinacol	**4**	Ph_2CO	Ph_2CHOH	**1**
1	Ph_2CO[c]	Rayonet[d]	15 min	81	80	47	50	[e]	2	1
2	Ph_2CO[c]	LJ[f]	ca. 50 μs	41	70	20	46	[e]	16	18
3	**2**[g]	Rayonet[h]	30 min	52	90	55	4	39	1	1
4	**2**[g]	LJ[f]	ca. 50 μs	28	80	37	5	51	6	1

[a] Detected by HPLC, error ±5% of stated value; MB stands for mass balance. — [b] Normalized to 100%, relative to $Ph_2C^{\bullet}OH$ (**3**). — [c] 8.77×10^{-4} M solution in EtOH. — [d] Irradiation for 15 min with 300-nm lamps. — [e] Substrate. — [f] Single passage through focal region of the argon-ion laser, 3.5–3.6 W all-UV lines (λ = 334, 351, 364 nm), 100-μm capillary. — [g] 1.04×10^{-2} M in EtOH; in these reactions PhCHO (16% in the LJ, 63% in the Rayonet) and PhCOCOPh (84% in the LJ, 37% in the Rayonet) were also detected. — [h] Irradiation for 30 min with 350-nm lamps.

Discussion

In inert solvents, the ground-state reaction of the radical **3** is dimerization to benzpinacol (Scheme 1). By using benzhydrol as hydrogen donor, two radicals **3** are generated by one benzophenone triplet. This pair of radicals dimerizes subsequently, so that under low-intensity conditions benzhydrol and benzophenone are consumed in equal amounts (Table 1, entry 1). It is known that upon excitation of the radical **3** to its excited state **3***, it fragments into an H atom and benzophenone[7,9].

This fragmentation is also achieved in the laser-jet mode and competes with the ground-state dimerization. The photolytic regeneration of benzophenone results in nearly unchanged amounts of this starting material, but appreciable consumption of the benzhydrol. Thus, benzhydrol is oxidatively dimerized to benzpinacol by the help of benzophenone. The fragmentation of the radical **3*** becomes more evident when catalytic amounts of benzophenone are used (Table 1, entry 4), conditions which lead to substantial growth of benzophenone.

The expelled hydrogen atoms form molecular hydrogen, which has been confirmed by Raman spectroscopy[7a]. In the laser-jet experiment gaseous products cannot be detected since the reaction is performed in an open system. For this reason the quantification of the amount of molecular hydrogen formed is for experimental reasons difficult; however, the small amounts of biphenyl suggest the intervention of H atoms, which were trapped by benzene. In a control experiment, benzophenone alone was photolysed in benzene in the laser jet, and no biphenyl was formed under these conditions, which indicates that H abstraction by triplet benzophenone from benzene[7b] to generate phenyl radicals is not an effective pathway in the laser-jet photolysis. Thereby we have established that excitation of the radical **3** by the continuous-wave argon-ion laser is feasible under the laser-jet photolysis conditions.

In ethanol, a more complex situation prevails in that the solvent-derived 1-hydroxyethyl radical is produced through H abstraction by triplet benzophenone or the excited $Ph_2C^{\bullet}-OH$ radical (**3***). The 1-hydroxyethyl radical can couple with the radical **3** to form pinacol **4** and ketone **1**. The ratio of the unsymmetric pinacol **4** to benzpinacol depends on the alcohol used as solvent, e.g. in 2-propanol mainly benzpinacol is formed whereas in ethanol and methanol the unsymmetric pinacol dominates[1].

Ketone **1** and benzhydrol are formed in increased amounts when the irradiations are conducted in the laser-jet mode, which indicates that these products are generated by a two-photon process. A similar increase in benzhydrol as product was observed in the Rayonet versus laser-jet irradiations in which the radical **3** was generated independently by α cleavage of ketone **2** in ethanol.

Benzhydrol is formed by H abstraction of radical **3** from a second radical **3** or from ethanol as possible H donors. The first possibility, namely disproportionation of two $Ph_2C^{\bullet}-OH$ radicals, a feasible process at high concentrations, cannot be a significant pathway because such disproportionation should also take place in the low-intensity irradiations. For example, in the Rayonet (low intensity) the intermolecular reaction of two radicals **3** is exclusive dimerization to benzpinacol. In the laser-jet mode higher concentrations of radicals **3** are obtained, but this cannot influence their selectivity.

The second possibility, the H abstraction from ethanol, is at least 7 kcal/mol endothermic for the ground-state $Ph_2C^{\bullet}-OH$ radical, as estimated from Benson's ΔH_f^0 increments[11]. The necessary energy for this thermal uphill process is presumably available in the electronically excited radical **3*** to effect hydrogen-atom abstraction. Furthermore, in its excited state the $Ph_2C^{\bullet}-OH$ radical may be a more electrophilic radical and possess a higher propensity for abstracting an α-hydrogen atom from ethanol.

In the formation of the ketone **1** four possible reaction partners have to be considered for the 1-hydroxyethyl radical, namely benzophenone and radical **3** in their ground and excited states. The attack of the 1-hydroxyethyl radical on benzpinacol to form radical **3** and the precursor of ketone **1** was according to Benson's increments[11] estimated to be ca. 97 kcal/mol, and this strongly endothermic process can therefore be neglected. First, the radical **3** and benzophenone will be considered in their ground states. Ground-state radical **3** couples with a 1-hydroxyethyl radical to the unsymmetric pinacol **4**. Thus, the cross-coupled pinacol **4** is the main product in the low-intensity photolysis. Again, at higher concentrations of both radicals it is unreasonable to presume that their selectivities are altered, and consequently it is unlikely that the ground-state radical **3** is the precursor to the *para*-coupling product **1**. Moreover, under the low-intensity conditions only traces of this ketone **1** were observed, so that the ground-state benzophenone can hardly be the substrate for the formation of the *para*-coupling product **1**. The predominance of the solvent-derived products pinacol **4** and ketone **1** in the laser-jet can be rationalized in terms of the higher concentrations of the intermediary radicals **3** and 1-hydroxyethyl radicals, which favor cross coupling to pinacol **4** and ketone **1** over self-termination to benzpinacol.

As the remaining reaction partners for the 1-hydroxyethyl radical to form ketone **1** we consider the excited states of either benzophenone or the radical **3**. Since triplet benzophenone should be deactivated quickly by H abstraction from ethanol (the solvent) before coupling with a 1-hydroxyethyl radical, it seems most reasonable that the latter couples with an excited radical **3***. This is likely in view of the fact that the excited radical **3*** is long-lived enough (4 ns[7]) to allow intermolecular reactions.

Furthermore, AM1 calculations[12] suggest that the spin density for the ground-state radical **3** is highest at the hydroxy-bearing carbon atom, whereas in the first excited state **3*** it is highest at the *para* position. These theoretical results provide a rationale for the preference in pinacol **4** formation from the ground state and the *para*-coupling product **1** from the excited state of the $Ph_2C^{\bullet}-OH$ radical. After coupling in its *para* position, the aromaticity is regained by dehydrogenation to ketone **1**.

The *para*-coupling product **1** is only formed to a significant extent in the laser-jet reaction of benzophenone in ethanol. Thus, when radical **3** was generated by α cleavage from ketone **2**, no increase of *para*-coupling product **1** was found in the laser-jet mode, over and beyond that obtained in the Rayonet irradiation. This is due to the low 1-hydroxyethyl radical concentration under these photolysis conditions, because the bimolecular reaction of an excited radical $\mathbf{3}^*$ and a 1-hydroxyethyl radical requires sufficiently high concentrations (at least micromolar) of such short-lived transients. It is also for this reason why in the low-intensity irradiation of benzophenone (Table 2, entry 1) only traces of ketone **1** are formed.

Thus, the concentration of 1-hydroxyethyl radicals is sufficiently high to form the unsymmetric pinacol **4** (main product) with abundantly available ground-state $\mathrm{Ph_2C^{\bullet}-OH}$ radical, but not high enough to encounter the sparingly present excited $\mathrm{Ph_2C^{\bullet}-OH^*}$ species to generate the *para*-coupling product **1**. Only in the laser-jet photolysis of benzophenone in ethanol are the concentrations of both transients high enough (at least micromolar) to form the two-photon product **1**.

With the help of the laser-jet technique we have aquired valuable results on the two-photon chemistry of the $\mathrm{Ph_2C^{\bullet}-OH}$ radical by conducting detailed product studies. In inert solvents the excited species $\mathrm{Ph_2C^{\bullet}-OH^*}$ exhibits an intramolecular reaction (H expulsion), while in the H-donating solvent ethanol also intermolecular chemistry of the excited transient $\mathbf{3}^*$ was observed. Thus, the excited $\mathrm{Ph_2C^{\bullet}-OH^*}$ radical readily abstracts H from ethanol to form benzhydrol. Additionally, $\mathrm{Ph_2C^{\bullet}-OH^*}$ couples at its *para* position with the transient 1-hydroxyethyl radical to form ketone **1**. This unprecedented result implies an unusual case of intermolecular chemistry of a short-lived radical transient with an electronically excited radical.

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Experimental

Materials and General Techniques: Benzophenone and benzhydrol were recrystallized twice from ethanol before use. Ketone **2** was prepared and purified according to the literature[13]. The HPLC analyses were carried out on a Kontron analytical system (T-414 pumps, Uvikon 720LC spectrometer, and an Anacomp 220 integrator), equipped with an RP-8 reversed-phase column by using ternary solvent mixtures of water (40%), MeOH (40%) and CH_3CN (20%) as eluent. Detection of the products was performed at $\lambda =$ 215 nm. The Uvikon spectrometer was also used for the determination of the spectra by HPLC/UV. GC: Carlo Erba HRGC, equipped with an SE54 or an OV1 fused-silica column, both 30 m in length. NMR: Bruker AC 250.

Low-Intensity Photolyses: Irradiations were carried out in Schlenk tubes. The solutions were degassed by purging with a slow stream of dry argon for 20 min and irradiated in a Rayonet Photochemical Reactor [RPR (75 W, 110 V)] of the Southern UV Company, equipped either with 300- or 350-nm lamps. The 5-ml samples were irradiated for the time stated in the tables.

High-Intensity Photolyses: The experimental setup is described in recent publications[10]. The beam of the INNOVA 100 argon-ion laser was focussed by means of a quartz lens ($f =$ 80 mm) onto a free-falling liquid stream of the photolysis solution, which was generated by passing the solution through a 100-µm capillary with the help of a Bischoff 2200 HPLC pump and maintained therewith. The samples were degassed by purging with a slow stream of dry argon for 20 min. The irradiation chamber was kept under a positive argon pressure. In the continuous mode (multiple cycles), the substrate solution was pumped by drawing from and returning to the same reservoir. When the substrate solutions were passed only once through the focal point (single cycle), fresh stock solution was drawn from an external reservoir. For HPLC analysis, aliquots of the photolysate were drawn from the collecting vessel.

Product Studies: Quantitative product studies were performed by HPLC with the help of 1,2-dicyanobenzene as internal standard. The unsymmetric pinacol **4**[11] was isolated from an irradiated solution of benzophenone in ethanol and identified by its ^{1}H- and ^{13}C-NMR spectra. Ketone **1** was synthesized according to a standard Grignard reaction between 2-(4-bromophenyl)-2-phenyldioxolane[14] and acetaldehyde; its ^{1}H-NMR spectrum was identical to that reported in literature[15]. All other products were identified by coinjection and comparison of their UV spectra with authentic materials. Biphenyl was detected by capillary GC, for which SE54 and OV1 fused-silica columns were used, both 30 m in length.

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