PERKIN 2

Multiple-photon† chemistry in the laser-jet: photochemistry of the 4-biphenylmethyl radical

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In laser-jet (LJ) photolysis (high intensity) of the ether 4-(4-benzoylphenoxymethyl)biphenyl 1 a two-photon process is observed in CCl_4 to yield 4-(chloromethyl)biphenyl 5 as product (3%), while the one-photon product is 4-biphenylaldehyde 7 (100% in conventional photolysis *versus* 97% in laser-jet photolysis). In ethanol, the results suggest a three-proton reaction in which 4-(ethoxymethyl)biphenyl 6 is produced in appreciable amounts (18%) in addition to the one-photon product 1,2-bis(4-biphenyl)ethane 4, the latter as the major product (82%). It is proposed that under high-intensity LJ photolysis conditions the electronically-excited 4-biphenylmethyl radical 2* is photoionized to the 4-biphenylmethyl cation 2^+ and that the latter is trapped by ethanol to give the 4-biphenylmethyl ether 6.

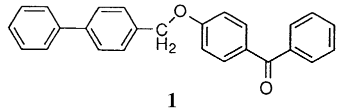
Introduction

The 4-biphenylmethyl radical **2** has for some time been the subject of photophysical studies.[1,2] This benzyl-type radical **2** has a strong absorption band centred at 326 nm,[2] which makes it a suitable substrate for laser-jet experiments,[3] especially at the 333 nm line available in the argon-ion laser (333, 351, 364 nm). For other well-studied arylmethyl radicals, generated upon irradiation of arylmethyl halides with pulsed lasers (two-colour experiments), photoionization to aryl cations was demonstrated by transient UV spectroscopy.[4,5] Similar multiple-photon chemistry is expected for the 4-biphenylmethyl radical **2**.

We report here that under high-intensity conditions of laser-jet photolysis of 4-(4-benzoylphenoxymethyl)biphenyl **1** the electronically-excited 4-biphenylmethyl radical **2*** is produced. Under further excitation **2*** is transformed to the 4-biphenylmethyl cation $\mathbf{2}^+$ by electron transfer, a process that requires several photons.

Results

The photolysis products, which are derived from the biphenylmethyl **2** and the 4-(benzoyl)phenoxy **3** radicals generated on C–O homolysis of ether **1**, are outlined in Scheme 1 and the product studies summarized in Table 1. The photolysis of 4-(4-benzoylphenoxymethyl)biphenyl **1** in CCl_4 solution afforded the chloride **5** and the aldehyde **7** as the products. A light intensity dependence of the product distribution was observed for 4-(chloromethyl)biphenyl **5**, since it was absent at low intensity, but detectable amounts for identification were found at high intensities (Table 1, entries 1 and 2). Although the process is inefficient (3%), these results indicate that multiple-photon chemistry is operating under the laser-jet conditions (high intensity).[6] Aldehyde **7**, essentially the exclusive product in CCl_4, is observed both under low- and high-intensity conditions (Table 1, entries 1 and 2).



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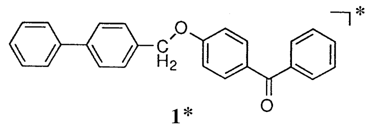

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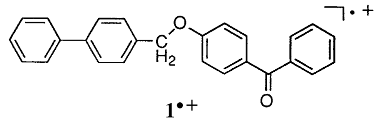

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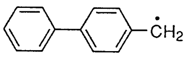

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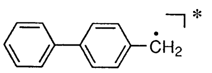

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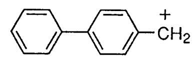

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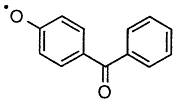

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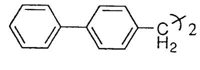

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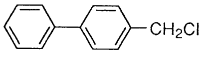

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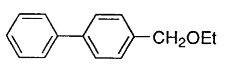

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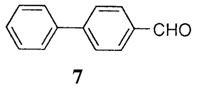

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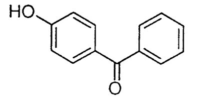

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To assess the origin of the aldehyde **7** in the low- and high-intensity photolyses, the ether **1** was treated with the one-electron oxidant bis(4-bromophenyl)(2,4-dibromophenyl) aminium hexachloroantimonate, known as 'Magic Green' ($E_0 = 1.42$ V),[7] in $CDCl_3$ and a dry argon gas atmosphere. At 9% conversion, the aldehyde **7** was the exclusive product besides 4-hydroxybenzophenone **8**.

In ethanol, the product composition of the ether **1** photolysis was considerably simpler (entries 3 and 4) than in CCl_4. The

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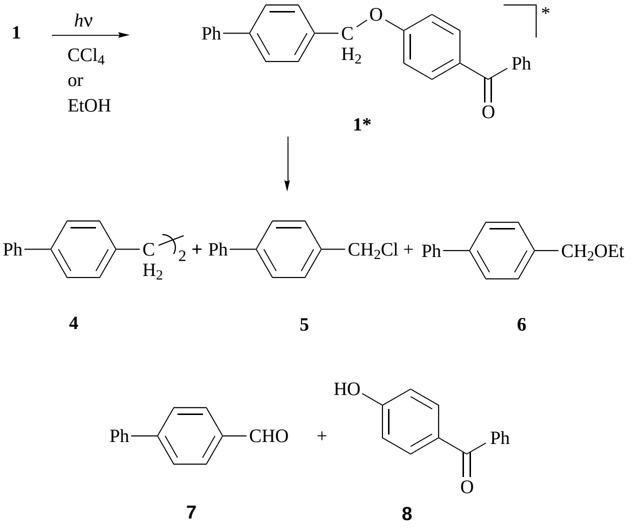
† A *multiple-photon* reaction refers to the sequential absorption of more than one photon by intermediary chemical species, in contrast to a *multiphoton* process in which two or more photons are absorbed simultaneously to produce a higher excited spectroscopic state.

Table 1 Product studies of the conventional (low intensity) and laser-jet (high intensity) photolyses of biphenyl ether **1** in carbon tetrachloride and in ethanol

Mode	Solvent	conv.[a] (%)	mb[a] (%)	Product distribution[a,b] (%)			
				4	**5**	**6**	**7**
Laser, widened beam	CCl_4	33	78	—	—	—	100
Laser-jet	CCl_4	4	95	—	3	—	97
Laser, widened beam	EtOH	62	69	100	—	—	—
Laser-jet	EtOH	29	79	82	—	18	—

[a] Conversion (conv.) of ether **1**, mass balance (mb) of products (deficit represents undefined and/or undetected material) and product distribution were determined by ^{1}H NMR spectroscopy, error 5% of stated value; 4-hydroxybenzophenone **8** was formed quantitatively. [b] Normalized to 100%.



Scheme 1

dimer **4** was formed under low- as well as high-intensity conditions. It was essentially the only product in the conventional photolysis (entry 3), while in the LJ experiment the ether **6** was additionally formed as a minor product in substantial (18%) amounts (entry 4).

Discussion

The mechanism for the single-photon process (conventional laser photolysis) is presented in Scheme 2, together with the chemical oxidation of ether **1** by 'Magic Green', while the multiple-photon reaction (laser-jet photolysis) is displayed in Scheme 3.

In the low-intensity experiments under conventional laser photolysis in CCl_4 solution, the electronically excited ether **1*** engages in electron transfer with CCl_4 (Scheme 2) to produce the radical cation $\mathbf{1}^{\cdot+}$ (ionization of the electron-rich biphenyl π system) and the $CCl_4^{\cdot-}$ radical anion. The latter has been established to dissociate readily into chloride ions and trichloromethyl radicals.[8] The radical cation $\mathbf{1}^{\cdot+}$ deprotonates and further oxidation to its cation, followed by trapping with adventitious water, leads to 4-biphenylaldehyde **7** and the phenol **8**. The fact that chemical oxidation of the ether **1** by 'Magic Green' afforded exclusively the aldehyde **7** and phenol **8** provides experimental support that the proposed photo-induced electron-transfer process is operating.

4-Biphenylaldehyde **7** also appears as the major product in CCl_4 in the laser-jet photolysis (entry 2); however, in contrast to conventional photochemistry at low intensity (Scheme 2), 4-(chloromethyl)biphenyl **5** was additionally observed under high-intensity conditions, although in low (3%) yield. As demonstrated previously for other arylmethyl radicals,[3] a multiple-photon process is involved, in which the intermediary 4-biphenyl radical **2** is photoionized by electron transfer with CCl_4 (Scheme 3).

The necessity for electronically-excited arylmethyl radicals in the photoionization with CCl_4 was demonstrated by Johnston and Scaiano through time-resolved laser-flash photolyses of the 1-naphthylmethyl radical.[9] Thus, the excited radical was quenched by CCl_4 and electron transfer was demonstrated by its reaction with Methyl Viologen.[9]

In ethanol as solvent, a completely different product composition is obtained for both conventional as well as laser-jet photolysis (entries 3 and 4). Mechanistically significant is the fact that in both the conventional and laser-jet photolysis modes no 4-biphenylaldehyde **7** was observed. This underscores the fact that CCl_4 is essential for the photo-induced electron transfer, while alcohols do not serve as effective electron acceptors. Moreover, it confirms that oxidation of the intermediary radical **2** by molecular oxygen to the aldehyde **7** cannot be a significant route because it should occur with nearly equal facility in CCl_4 and EtOH.

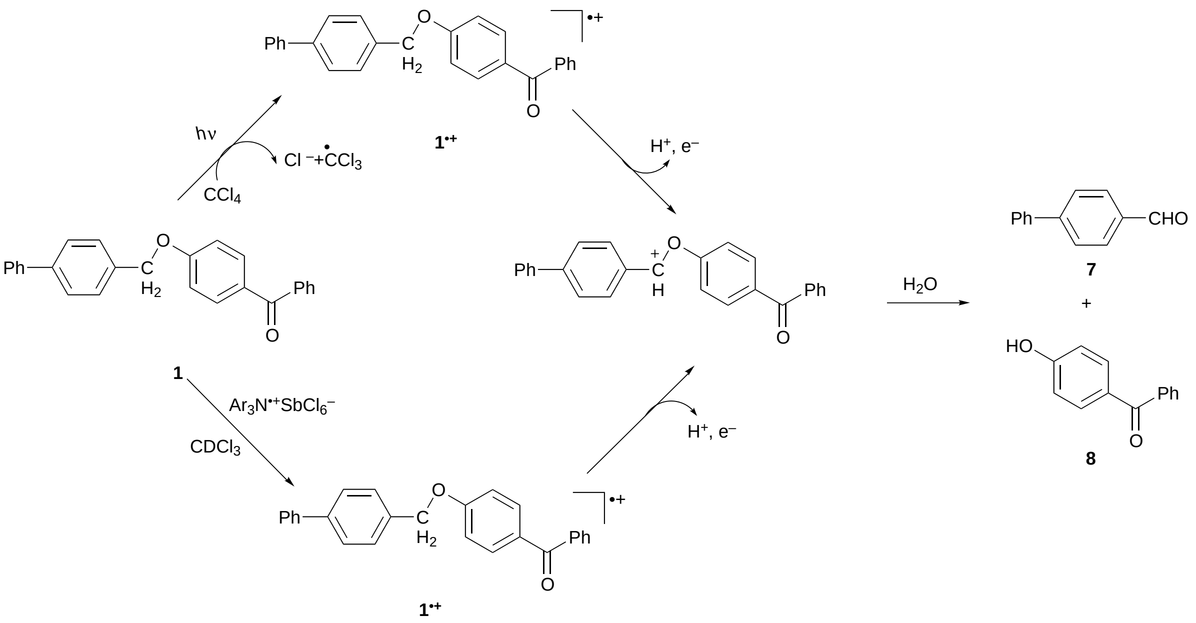
The fate of the radicals **2** on laser-jet photolysis in ethanol is that appreciable amounts (18%) of the new ether **6** (Table 1, entry 4) are produced, besides the conventional dimer **4** as major product (82%). Since electron transfer from the excited radical **2*** to ethanol, as in the case of CCl_4, is not feasible, we propose that photoionization competes with dimerization of the radical **2** to generate the cation $\mathbf{2}^+$ (Scheme 3), analogous to our previous study on the benzhydryl radical.[3] The cation $\mathbf{2}^+$ is subsequently nucleophilically trapped by ethanol to afford the ether **6**. Such photoionization of arylmethyl radicals has been documented[4,5] and provides experimental support for this mechanism. Thus, in laser-jet photolysis of the starting ether **1** in ethanol at least three photons are required to generate the 4-biphenylmethyl cation ($\mathbf{2}^+$) (Scheme 3). The first photon is required for C–O bond homolysis in the ether **1** to afford the benzyl-type radical **2**, the second for excitation of the latter radical, and finally at least a third photon for ionization of the excited radical **2*** to its cation $\mathbf{2}^+$.

This underscores the efficiency of the LJ technique in achieving high photon densities and in allowing detailed product studies for such multiple-photon reactions. Thus, the LJ mode of operation constitutes a valuable complementary technique for time-resolved laser flash photolysis with pulsed lasers. The latter offers valuable mechanistic data in terms of absorption spectra, lifetime and rate constants of short-lived transients, but normally insufficient amounts of products are formed to conduct the essential product studies.

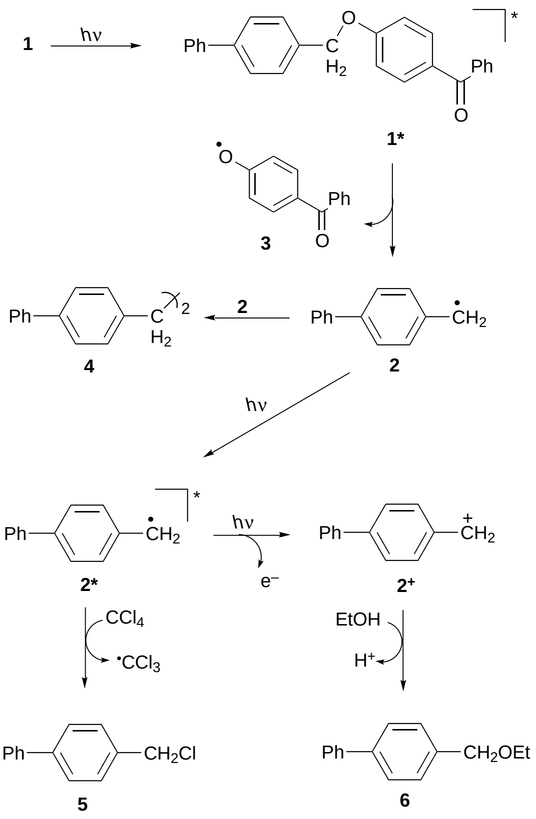
Experimental

General aspects

Ethanol and carbon tetrachloride were distilled. Immediately before photolysis, CCl_4 was passed through an alumina column to remove traces of acid. All solutions were degassed by purging with a slow stream of dry argon gas for 45 min before irradiation. NMR spectra were recorded on a Bruker AC 200 or a Bruker AC 250 spectrometer. Quantitative product studies were determined by ^{1}H NMR analysis ($CDCl_3$) of the identified products directly on the product mixtures after removal of the solvent under reduced pressure (*ca.* 20 °C, 18 Torr). The IR



Scheme 2



Scheme 3

spectra were recorded on a Perkin-Elmer 1420 and the UV spectra on a Hitachi U-3200 spectrophotometer. Chloride **5**, aldehyde **7** and ketone **8** were prepared according to reported procedures.[10a,b]

Normal laser irradiations

These were carried out in a Schlenk tube by irradiation at the 333, 351 and 363 nm lines of the Coherent INNOVA 100 argon-ion laser (3.0 W over all UV lines), supplied with UV quartz optics. The beam was widened with a quartz lens ($f = 50$ mm) to a size of *ca.* 1 cm in diameter and the 20 cm^3 sample was irradiated for 15 min (ethanol) or 10 min (CCl_4) under an argon gas atmosphere.

Laser-jet irradiations

The experimental set-up, as described previously,[6a,b] was employed. The beam of the argon-ion laser (3.6 W over all UV lines) was focused by means of a quartz lens ($f = 80$ mm) onto a free-falling liquid jet of the photolysis solution. The free-falling liquid jet was generated by passing the substrate solution to be irradiated through a 50 µm capillary and maintained at a constant flow rate by means of a Bischoff 2200 HPLC pump. The irradiation chamber was kept under a positive argon gas pressure and the substrate solution was passed once (CCl_4) and four times (ethanol) through the focal region of the laser beam for the irradiation.

4-(4-Benzoylphenoxymethyl)biphenyl 1

A solution of 2.78 g (14.0 mmol) of 4-hydroxybenzophenone and 1.82 g (13.2 mmol) of potassium carbonate in 50 cm^3 of dry acetone was stirred for 5 min at room temperature (*ca.* 20 °C) and 3.00 g (12.1 mmol) of 4-bromomethylbiphenyl in 25 cm^3 of dry acetone was added slowly and the reaction mixture was allowed to reflux for 14 h. The solvent was removed under reduced pressure (*ca.* 20 °C, 18 Torr) and 50 cm^3 of distilled water was added. The aqueous solution was extracted with methylene chloride (3 × 20 cm^3), the organic phase was washed with saturated, aqueous Na_2CO_3 (2 × 20 cm^3), and with saturated, aqueous NaCl (2 × 20 cm^3), dried over $MgSO_4$ and the solvent removed under reduced pressure (*ca.* 20 °C, 18 Torr). After recrystallization from ethanol, 2.80 g (60%) of ether **1** was obtained as colourless needles, mp 122–123 °C, IR (KBr) ν/cm^{-1} 3000, 2920, 2840, 1640 (CO), 1580, 1280, 1240, 1165, 1065, 990; UV (CH_3CN) λ/nm (log ε) 283 (3.77), 336 (2.40); ^1H NMR ($CDCl_3$, 250 MHz) δ 5.20 (s, 2 H), 7.08 (d, J 8.9 Hz, 2 H), 7.3–7.66 (m, 12 H), 7.78 (m, 2 H), 7.85 (m, 2 H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 69.9 (t), 114.4 (d), 127.1 (d), 127.4 (s), 127.8 (d), 128.0 (d), 128.2 (d), 128.8 (s), 129.1 (d), 129.7 (d), 129.9 (s), 130.4 (d), 131.9 (d), 132.6 (d), 135.1 (s), 138.1 (s), 162.3 (s), 195.0 (s). Calc. for $C_{26}H_{20}O_2$ (364.4): C, 85.69; H, 5.53. Found: C, 85.26; H, 5.27.

1,2-Bis(4-biphenyl)ethane 4

A suspension of 900 mg (4.44 mmol) of 4-chloromethylbiphenyl **5** and 603 mg (10.8 mmol) of iron powder in 20 cm^3 of water was allowed to reflux for 3 h. Methylene chloride (10 cm^3) was added and the organic phase was washed with water (3 × 10 cm^3), dried over $MgSO_4$ and the solvent removed by distillation (42 °C, 760 Torr). Unreacted starting material was removed under reduced pressure (bp 188 °C, 0.1 Torr), 20 cm^3 of methylene chloride was added to the residue, the solution was filtered through a short silica gel (10 g) column, and the solvent again removed by distillation (42 °C, 760 Torr). After recrystallization from benzene, 300 mg (40%) of product **4** was obtained as colourless needles, mp 194–196 °C. IR (KBr) ν/cm^{-1} 3025, 2920, 2860, 1590, 1500, 1460, 1390, 1075; ^1H NMR ($CDCl_3$, 200 MHz) δ 3.03 (s, 4 H), 7.21–7.83 (m, 18 H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 37.5 (t), 126.9 (d), 127.0 (d), 127.1 (d), 128.7 (d), 128.9 (d), 138.9 (s), 140.8 (s), 141.0 (s). Calc. for $C_{26}H_{22}$ (334.5): C, 93.37; H, 6.63. Found: C, 93.63; H, 6.35.

4-(Ethoxymethyl)biphenyl 6

A solution of 1.00 g (4.93 mmol) of 4-(chloromethyl)biphenyl **5** in 10 cm^3 of absolute ethanol was added to a solution of 127 mg (5.51 mmol) of sodium dissolved in 10 cm^3 of absolute ethanol. The solution was refluxed for 3.5 h, the solvent was removed under reduced pressure (*ca.* 20 °C, 18 Torr) and then 10 cm^3 of cold water was added to the residue. The solution was neutralized by acetic acid, the aqueous phase was extracted with ether (3 × 10 cm^3) and the combined organic layers were dried over $MgSO_4$. The solvent was removed by distillation (35 °C, 760 Torr) and fractional distillation of the residue under reduced pressure afforded 610 mg (58%) of pure ether **6** as a colourless oil, bp 102–103 °C/0.1 Torr. IR (NaCl) ν/cm^{-1} 3010, 2840, 1475, 1450, 1365, 1345, 1090, 1000, 820; ^1H NMR ($CDCl_3$, 200 MHz) δ 1.41 (t, *J* 7.0 Hz, 3 H), 3.70 (q, *J* 7.0 Hz, 2 H), 4.67 (s, 2 H), 7.53 (m, 5 H), 7.72 (m, 4 H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 15.1 (q), 65.6 (t), 72.2 (t), 126.7 (d), 126.9 (d), 127.1 (d), 128.0 (d), 128.6 (d), 137.5 (s), 140.3 (s), 140.7 (s). Calc. for $C_{15}H_{16}O$ (212.3): C, 84.87; H, 7.60. Found: C, 84.62; H, 7.87.

Oxidation of ether 1 by Magic Green

To a solution of 20.0 mg (54.9 mmol) of ether **1** in 0.7 cm^3 of $CDCl_3$, passed through an alumina column (*ca.* 2 g) shortly before use, was added 17.0 mg (19.3 mmol) of bis(4-bromophenyl)(2,4-dibromophenyl)aminium hexachloroantimonate (Magic Green)[4] under an argon atmosphere. The mixture was well shaken and immediate analysis by ^1H NMR spectroscopy showed aldehyde **7** and ketone **8** as exclusive oxidation products (conversion 9%, mass balance >95%).

Acknowledgements

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