

Microwave photochemistry III: Photochemistry of 4-*tert*-butylphenol

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Received 1 December 2004
Available online 23 March 2005

Abstract

Influence of UV and combined MW–UV irradiation on 4-*tert*-butylphenol (4TBP) transformation was investigated in the presence and in the absence of sensitizers with different value of singlet and triplet energy and in the presence of solvents with different polarity. Irradiation by UV and also by MW–UV gave C–O and C–C products: 4',5'-di-*tert*-butyl-2-hydroxydiphenyl ether (**1**) (*ortho*-O), 5,5'-di-*tert*-butylbiphenyl-2,2'-diol (**2**) (*ortho*–*ortho*) and 2TBP as an isomerization product. Their ratio depends upon the nature of solvents and sensitizers used. In non-polar solvents (hexane, heptane, toluene), direct 4TBP radiation led to the formation of products **1**, **2** and 2TBP where *ortho*–*ortho* dimer **2** is predominant over *ortho*-O ether **1**. In acetonitrile *ortho*–*ortho* dimer **2** was selectively formed under UV and MW–UV irradiation. In 1,4-dioxane and in methanol, no product formation was observed. Influence of solvent polarity (acetone, hexane) on the relative products distribution of 4TBP photoreaction was also observed in the presence of sensitizers: acetone, naphthalene, acetophenone and benzophenone. The acetone-sensitized reaction was found to give all three products: *ortho*-O ether **1**, *ortho*–*ortho* dimer **2** and 2TBP where *ortho*-O ether **1** is predominant. In the presence of singlet sensitizer naphthalene, the reaction of 4TBP in hexane gave mainly *ortho*-O ether **1** and 2TBP, whereas *ortho*–*ortho* dimer **2** was not found. Triplet-sensitized reaction with acetophenone in hexane led selectively to *ortho*-O ether **1**, while with benzophenone gave moreover 2TBP and its *ortho*–*ortho* **3** and *ortho*–*para* **4** dimers.

Keywords: Microwave photochemistry; Electrodeless discharge lamp; 4-*tert*-Butylphenol

1. Introduction

Microwave photochemistry [1] is an interesting part of microwave chemistry and photochemistry. Its fundamental principles have recently been described by us [2–5]. In the past seven years, over 40 papers dealing with combination of the microwave (MW) and ultraviolet (UV) irradiation have been published [1,6].

The UV irradiation can be generated either by classical method using mercury lamps or by our method using the electrodeless discharge lamps (EDLs). The MW field generates UV discharge in the EDL with the resulting simultaneous UV and MW irradiation of the sample. The new MW–UV system for the application in organic synthesis was developed by us [4,7]. The emission characteristics of the mercury EDL have been published [8].

The electron distribution of molecules in an excited state has the changes that differ from those in the ground state [9,10]. The dipole moment changing that can be affected by MW may be connected with changes in solute–solvent interactions and acidity. Therefore, the study of MW–UV combination was performed.

Phenols and their *tert*-butyl derivatives [11] are important probe molecules for investigating some of the fundamental photoprocesses occurring in many chemical and biological systems. The sterically hindered phenols with *tert*-butyl bulky substituents are often used as antioxidants.

Oxidation of 4TBP with cupric salts [12], potassium ferricyanide [13], Cu(II)-ethylene diamine complexes [14,15] and horseradish peroxidase [16] gave two C–C and C–O coupling products. The ratio of phenylene and oxyphenylene units in the product, i.e. coupling selectivity, was controlled by changing the hydrophobic parameters of the solvent.

The steady UV irradiation of *p*-cresol [17] in water yielded three products: C–C and C–O dimers as well

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as 4-methylcatechol. The catechols arise in part from C–O dimer and in part by direct hydroxylation but not from C–C dimer. The photooxidation of *p*-phenylphenol [18] by excited uranyl ion was investigated in aqueous solution and led, via intermediate phenoxyl radical, to C–C dimer, no formation of quinone being observed. Direct irradiation of 2,4,6-tri-*tert*-butylphenol in hexane and acetone [19] gave only de-*tert*-butylated products, but no corresponding rearranged products or dimers were found.

The photochemical transformation of 2TBP in the presence and in the absence of sensitizers and in the solvents with different polarity has been investigated by us [20]. Irradiation gave three C–C dimers, their ratio depended upon the nature of solvents and sensitizers used. However, the fundamental influence of MW–UV radiation on the relative products distribution and the reaction selectivity was not observed.

In the present study we describe the influence of UV and MW–UV irradiation on 4TBP transformation in the presence and in the absence of sensitizers with different value of singlet and triplet energy and in the presence of solvents with different polarity.

2. Experimental

2.1. Equipment

Microwave experiments were accomplished [20] in the modified MW oven (Whirlpool M435, 900 W) operating at 2.45 GHz. Classical immersion-well photoreactor (300 ml) contained the medium-pressure UV lamp (Teslamp, RVK 125). Electrodeless discharge lamps (EDLs) [20] were manufactured in Teslamp (Prague, Czech Republic).

GC was performed using an HP 5890 instrument with HP-5 column (0.2 mm, 25 m) and nitrogen as a carrier gas. The results were corrected and normalized by the applying FID response-correction factors obtained from calibration runs (4TBP was chosen as reference). Reproducibility of peak areas was not worse than 5%. GC/MS analysis was accomplished on an HP 6890 instrument with mass detector HP 5973 (70 eV), DB-5 ms column (0.25 mm, 30 m) and helium as a carrier gas.

¹H NMR spectra were recorded on Varian Mercury VX300 instrument [20].

2.2. Chemicals

Acetophenone (99%), biphenyl-2,2'-diol (99%), 4-*tert*-butylphenol (99%), naphthalene (98%) (all from Sigma–Aldrich); aluminum oxide (Brockmann I, basic, pH 9.5), aluminum chloride (99%), benzophenone (99%) (all from Fluka). Solvents (acetone, acetonitrile, benzene, dichloromethane, 1,4-dioxane, diethyl ether, heptane, hexane, methanol, pentane, toluene) were purified by distillation (all p.a., Lachema, Brno, Czech Republic). The quality of all solvents was verified by UV/vis spectrophotometer (Helios γ , Thermo Electron Scientific Instruments, USA) using the software package Vision32.

2.3. Photochemical and microwave-photochemical experiments

4TBP (1.8 g, 0.012 mol) in different solvents (300 ml, $c = 0.04 \text{ mol l}^{-1}$, Table 1) and/or with sensitizer (0.012 mol, Table 2) were irradiated for 2 h in the classical immersion-well photoreactor according to our previous work [20].

4TBP (1.2 g, 8 mmol) in different solvents (200 ml, $c = 0.04 \text{ mol l}^{-1}$, Table 1) and/or with sensitizer (8 mmol,

Table 1
Transformation of 4TBP by UV and combined MW–UV radiation in solvents with different polarity^a

Run	Solvent	Type of radiation	Relative products distribution (%) and concentration (mmol l^{-1}) ^{b,c}			R_1 [1]/[2]	Conversion ^c 4TBP (%)
			1	2	2TBP		
1	Hexane	MW–UV	22 (1.1)	61 (2.9)	17 (0.8)	0.36	12
2		UV	27 (1.3)	46 (2.2)	27 (1.3)	0.59	12
3	Heptane	MW–UV	29 (2.2)	58 (4.4)	13 (1.0)	0.50	19
4		UV	28 (1.2)	58 (2.6)	14 (0.6)	0.48	11
5	Toluene	MW–UV	34 (0.9)	60 (1.7)	6 (0.2)	0.57	7
6		UV	32 (0.7)	62 (1.2)	6 (0.1)	0.52	5
7	Acetonitrile	MW–UV	0	100 (4.0)	0	–	10
8		UV	0	100 (3.2)	0	–	8
9	1,4-Dioxane	MW–UV	0	0	0	–	0
10		UV	0	0	0	–	0
11	Methanol	MW–UV	0	0	0	–	0
12		UV	0	0	0	–	0

^a 4TBP concentration 0.04 mol l^{-1} ; irradiation time 2 h at reflux. MW–UV: experiments with the electrodeless discharge lamp (EDL) in microwave field; UV: experiments with conventional medium pressure Hg lamp.

^b The ratios were determined according to GC analysis; the reproducibility was $\pm 5\%$.

^c Quantification was established on normalizing peak areas applying detector response-correction factors.

Table 2
Transformation of 4TBP by UV and combined MW–UV radiation in the presence of sensitizers^a

Run	Solvent	Sensitizer	Type of radiation	Relative products distribution (%) and concentration (mmol ⁻¹) ^{b,e}			Conversion ^e 4TBP (%)
				1	2	2TBP	
1	Acetone	Acetone	MW–UV	77 (2.5)	19 (0.6)	4 (0.1)	8
2			UV	55 (2.0)	23 (0.8)	22 (0.8)	9
3	Hexane	Naphthalene	MW–UV	65 (1.0)	0	35 (0.6)	4
4			UV	66 (0.8)	0	34 (0.4)	3
5		Acetophenone	MW–UV	100 (4.0)	0	0	10
6			UV	100 (4.0)	0	0	10
7			MW–UV ^c	100 (3.2)	0	0	8
8		Benzophenone	MW–UV	33 (4.0)	0	51 + (6 + 10) [6.1 + (0.7 + 1.2)] ^d	30
9			UV	34 (4.5)	0	52 + (5 + 9) [6.8 + (0.7 + 1.2)] ^d	33

^a 4TBP concentration 0.04 mol l⁻¹; irradiation time 2 h at reflux; the molar ratio of 4TBP/sensitizer = 1:1.

^b The ratios were determined according to GC analysis; the reproducibility was $\pm 5\%$.

^c The molar ratio of 4TBP/acetophenone = 1:5.

^d The reaction mixture contained products **3** and **4** (Scheme 2).

^e Quantification was established on normalizing peak areas applying detector response-correction factors.

Table 2) was irradiated for 2 h by the EDL according to [20].

The photoproduct identification and analysis were described early [20].

2.4. Photoproduct **2** from 4TBP in acetonitrile under MW–UV irradiation (Table 1, run 7)

The crude photoreaction mixture was concentrated under reduced pressure (80 °C, 666 Pa) and steam distilled. Chromatography of yellow oil on 1.4 × 60 cm aluminum oxide column eluted with dichloromethane-hexane (1:1, v/v) mixture gave 73 mg (6%) of 5,5'-di-*tert*-butylbiphenyl-2,2'-diol (**2**) as viscous oil which was crystallized from benzene as a white solid, mp 207–209 °C (Ref. [13]: 210–211 °C).

The spectral characteristics of **2** were as follows: ¹H NMR (CDCl₃) δ : 1.42 (s, 18H, CH₃); 5.44 (bs, 2H, OH); 6.96 (m, 2H, arom 3-H); 7.29 (m, 2H, arom 6-H); 7.42 (m, 2H, arom 4-H) ppm (Ref. [12,13,16]). MS *m/z* (abund. %): 299 (6), 298 (30, M⁺), 284 (21), 283 (100, M–CH₃⁺), 228 (10), 227 (49), 134 (12), 106 (15), 57 (12, *t*-Bu⁺), 41 (6) (Ref. [21]).

2.5. Photoproduct **1** from acetophenone-sensitized reaction of 4TBP in hexane under MW–UV irradiation (Table 2, run 5)

The crude photoreaction mixture was concentrated under reduced pressure (80 °C, 666 Pa) and steam distilled. Chromatography of yellow oil on 1.4 × 60 cm aluminum oxide column eluted with hexane gave 69 mg (6%) of 4',5'-di-*tert*-butyl-2-hydroxydiphenyl ether (**1**) as viscous oil which was crystallized from pentane as colorless crystals, mp 63–65 °C (Ref. [13]: 62–64 °C).

The spectral characteristics of **1** were as follows: ¹H NMR (CDCl₃) δ : 1.26 (s, 9H, CH₃); 1.33 (s, 9H, CH₃); 5.35 (bs, 1H, OH); 6.95 (m, 2H, arom-2',6'); 7.00–7.11 (m, 3H, arom-

3,4,6); 7.38 (m, 2H, arom-3',5') ppm (Ref. [13,16]). MS *m/z* (abund. %): 299 (9), 298 (41, M⁺), 284 (25), 283 (100, M–CH₃⁺), 267 (4), 227 (17), 134 (16), 133 (4), 120 (7), 107 (4), 106 (16), 105 (4), 91 (5), 77 (4), 57 (5, *t*-Bu⁺).

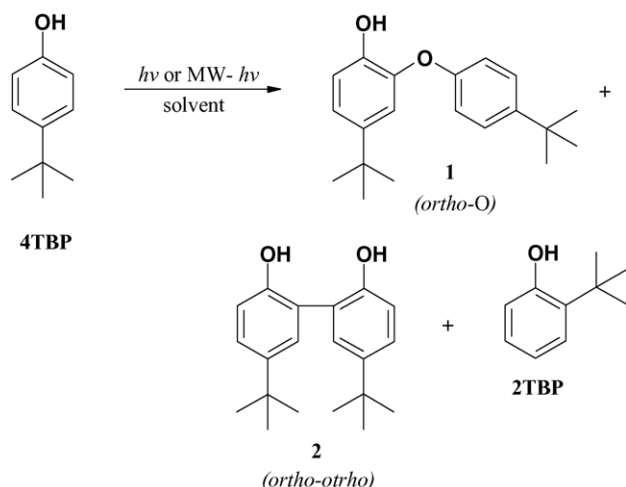
2.6. Dealkylation of 4',5'-di-*tert*-butyl-2-hydroxydiphenyl ether (**1**) and 5,5'-di-*tert*-butylbiphenyl-2,2'-diol (**2**)

The 4',5'-di-*tert*-butyl-2-hydroxydiphenyl ether (**1**) or 5,5'-di-*tert*-butylbiphenyl-2,2'-diol (**2**) (15 mg, 0.05 mmol), aluminum chloride (7 mg, 0.05 mmol) and benzene (1 ml) was stirred at room temperature overnight, worked up with ice and extracted with diethyl ether [19]. Concentration of the extracts in vacuo afforded yellow oils. The structures of the products were confirmed by mass spectra (NIST database). MS *m/z* (abund. %) (2-hydroxydiphenyl ether): 187 (13), 186 (100, M⁺), 185 (9), 169 (6), 157 (11), 131 (5), 129 (8), 128 (7), 115 (4), 109 (7), 81 (7), 80 (11), 78 (11), 77 (15), 52 (5), 51 (10), 39 (4). MS *m/z* (abund. %) (biphenyl-2,2'-diol): 187 (13), 186 (100, M⁺), 185 (14), 158 (22), 157 (36), 139 (15), 129 (11), 128 (16), 115 (9), 102 (4), 89 (4), 77 (5), 63 (5).

3. Results and discussion

The UV and MW–UV irradiation of 4TBP afforded C–O and C–C products (Scheme 1): 4',5'-di-*tert*-butyl-2-hydroxydiphenyl ether (**1**) (*ortho*-O), 5,5'-di-*tert*-butylbiphenyl-2,2'-diol (**2**) (*ortho*–*ortho*) and 2TBP as an isomerization product.

Photoproducts **1** and **2** were isolated by column chromatography on alumina (Sections 2.4 and 2.5), and the identifications were verified by NMR [12,13,16] and MS spectra [21]. Structures of *ortho*-O ether **1** and *ortho*–*ortho* dimer **2** were confirmed by dealkylation reaction with AlCl₃ [19] (Section 2.6) to afford 2-hydroxydiphenyl ether and biphenyl-2,2'-diol. The presence of 2TBP in photoreaction mixture was proved by GC/MS analysis.



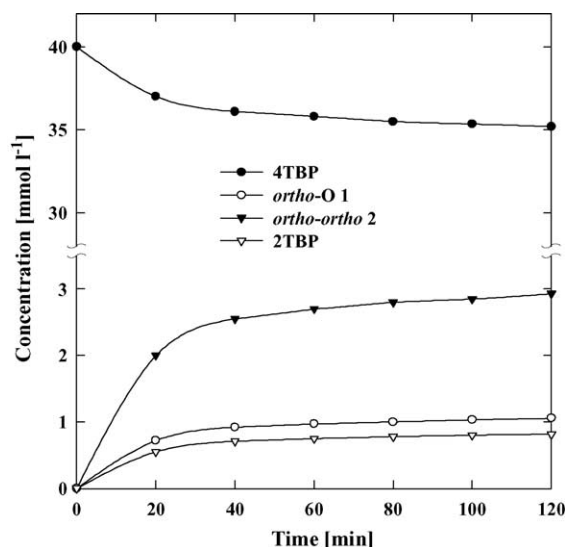
Scheme 1. Photoreaction products of 4TBP.

3.1. Influence of solvent polarity

Phototransformation of 4TBP by UV and MW–UV radiation was investigated in the presence of solvents (Table 1) with different polarity. The reaction mixture of 4TBP (0.04 mol l^{-1}) in various solvents was irradiated for 2 h at the reflux temperature. The results of individual experiments were compared with respect to the relative products distribution (%), concentration of the products (mmol l^{-1}) and to the ratio of products $R_1 = (\text{ortho-O}) \mathbf{1}/(\text{ortho-ortho}) \mathbf{2}$ (Table 1) in order to have a clear indication of the efficiency of the process. The major reason for low conversion of 4TBP (8–19%, Table 1) was probably the formation of colored by-products and their inhibition effect.

In non-polar solvents (hexane, heptane, toluene), direct 4TBP irradiation (Scheme 1) led to the formation of products **1**, **2** and 2TBP where *ortho-ortho* dimer **2** is predominant over *ortho-O* ether **1** (Table 1, runs 1–6). The Fig. 1 reports the concentrations (mmol l^{-1}) of 4TBP and products **1**, **2** and 2TBP in time for MW–UV irradiation in hexane (Table 1, run 1). The 4TBP conversion 12% led to the final concentration of *ortho-ortho* dimer **2** 2.9 mmol l^{-1} , *ortho-O* ether **1** 1.1 mmol l^{-1} and 2TBP 0.8 mmol l^{-1} . This figure also shows that concentration of substrate and products are constant after 60 min of irradiation.

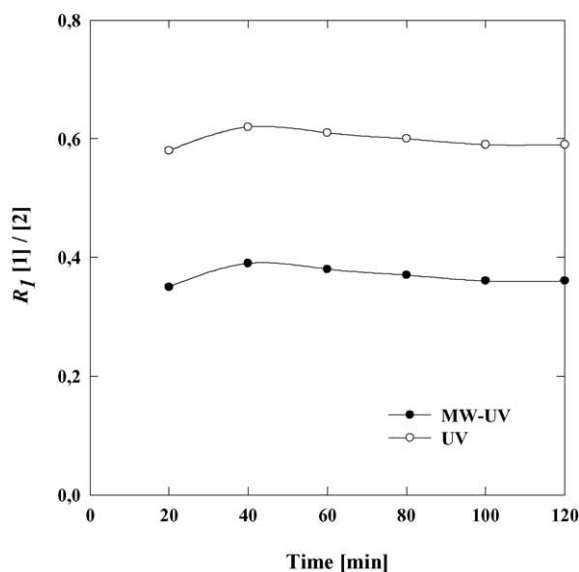
Time-dependence of R_1 for 4TBP in hexane under UV and MW–UV irradiation (Table 1, runs 1–2) is presented in Fig. 2. The interpretation of experimentally obtained values R_1 makes possible to assume that the ratio of products R_1 is time-independent. Conversions of 4TBP after 2 h irradiation in hexane and heptane ranged from 11 to 19% (Table 1, runs 1–4). The slight effect of UV and MW–UV radiation on relative distribution of *ortho-ortho* dimer **2** and 2TBP was observed only for hexane (Table 1, runs 1–2, 61% versus 46%). Similar difference was found also in 2TBP irradiation [20] (for *ortho-ortho* dimer **3**, 45% versus 36%). These results can be explained by influence of the EDL on the local superheating of the low-boiling hexane (for 2TBP irradiation

Fig. 1. Concentrations of 4TBP and products **1**, **2** and 2TBP in time for MW–UV irradiation in hexane (Table 1, run 1).

at 20 °C only 25% of **3** was found [20]). The effect of MW irradiation on polar excited states of 4TBP in heptane and toluene was not observed (runs 3–6).

The irradiation of 4TBP was carried out also in toluene (Table 1, runs 5–6). Relative products distribution was comparable to that for hexane and heptane. Conversions of 4TBP were only 5–7% owing to high efficiency of toluene to absorb UV radiation in the region 230–260 nm [22]. Also the light performance of electrodeless lamp in toluene was decreased by formation of the yellow polymeric film on the lamp surface. Therefore it was necessary to clean the lamp envelope in intervals of 15–20 min.

Similarly, in the 4TBP oxidation with $\text{K}_3[\text{Fe}(\text{CN})_6]$ [13] two dimeric products **1** (32%) and **2** (68%) were yielded.

Fig. 2. Time-dependence of R_1 for 4TBP in hexane under UV and MW–UV irradiation (Table 1, runs 1, 2).

The product ratio was similar as for nonpolar solvents, however, no 2TBP was observed. The proportion of ether **1** was very much higher than in the comparable oxidations of *p*-cresol (2%). The influence of bulky *tert*-butyl group prevented *ortho*–*para* coupling (typical for *p*-cresol) so that no Pummerer's type ketone was found.

Irradiation of 4TBP in acetonitrile (Table 1, runs 7–8) led selectively only to *ortho*–*ortho* dimer **2**. The isomerization to 2TBP was not observed. The high product selectivity was probably affected by ability of acetonitrile to stabilize free radicals [23] by electron delocalization. The effect of UV and MW–UV radiation on the relative products distribution was not observed.

In 1,4-dioxane and methanol, no product formation was observed (Table 1, runs 9–12). The similar results were indicated for the direct irradiation of 2,4,6-tri-*tert*-butylphenol [19]. The dynamic viscosities of 1,4-dioxane (0.46 mPa s) and methanol (0.38 mPa s) at reflux temperature are higher than for other solvents (hexane 0.21 mPa s, acetonitrile 0.23 mPa s), therefore photoreaction and deactivation of phenoxyl radical **5** is significantly influenced by diffusion. The 4TBP is much less photoreactive in these solvents compare to 2TBP, because the 2TBP irradiation [20] in 1,4-dioxane (2–4% conversion) led to dimer **3**.

Under protic conditions, hydrogen bonds are formed with the hydroxyl group of the phenols [23]. Phenol acts as proton donor and, consequently, electronic charge is transferred from the solvent molecule to the phenolic oxygen, which stabilizes the phenol-excited state. Therefore, the fluorescence lifetime (τ_f) prolongation indicates the higher stability of the S_1 state in the presence of hydrogen bonds compared to the nonpolar or aprotic situation (for 4TBP: $\tau_f = 4.7$ ns in methanol versus $\tau_f = 1.4$ ns in cyclohexane) [24]. Compared to the phenol (5.2 ns versus 2.2 ns), the substitution by *tert*-butyl group in *para*-position only slightly affects the τ_f , however the *tert*-butyl substitution in one or two *ortho*-positions causes a drastic τ_f decrease (4.0–0.03 ns versus 0.46–0.05 ns).

3.2. Effect of sensitizers

Influence of solvent polarity (acetone, hexane) to the relative products distribution of 4TBP photoreaction (Table 2, runs 1–9) was also investigated in the presence of sensitizers: acetone, naphthalene, acetophenone and benzophenone. The absorption bands of 4TBP in tested solvents ($\epsilon_{277} = 2200 \text{ l mol}^{-1} \text{ cm}^{-1}$; Ref.: [25,26]) overlapped absorption bands of used sensitizers [27]. The phenol spectra are not changed with increasing temperature, indicating the absence of stable hydrogen bonded complexes [28].

Acetone-sensitized reaction (Table 2, runs 1–2) was found to give all three products: *ortho*-O ether **1**, *ortho*–*ortho* dimer **2** and 2TBP, where *ortho*-O ether **1** is predominant (under MW–UV radiation, run 1). The 2TBP contents are increased to 22% under UV radiation (run 2) and their ratio under UV and MW–UV irradiation were similar (22 to 4% in acetone

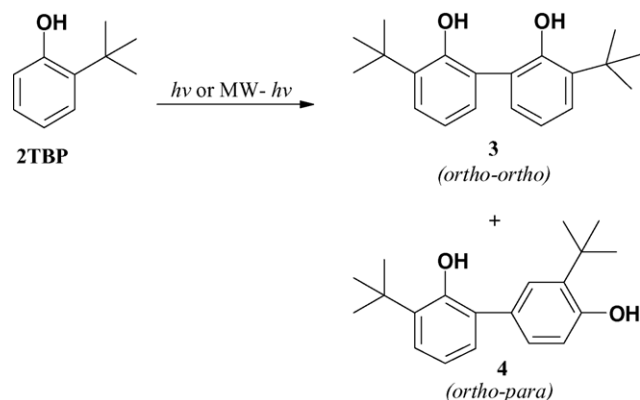
versus 27 to 17% in hexane, Table 1, runs 1–2). The relative products distribution was comparable to nonsensitized photoreactions (Table 1, runs 1–6). Acetone as a triplet sensitizer enhanced the amount of *ortho*-O ether **1**, the similar effect was also observed for acetophenone-sensitized photoreactions (Table 2, runs 5–7).

In the presence of singlet sensitizer naphthalene (Table 2, runs 3–4), the reaction of 4TBP in hexane gave mainly *ortho*-O ether **1** (65–66%) and 2TBP (34–35%), whereas *ortho*–*ortho* dimer **2** was not found. Irradiation led to the drop in conversion to 3% (run 4). The relative products distribution was different from the direct irradiation in hexane (Table 1, runs 1–2), therefore it was assumed that the photoreaction proceeds probably from the upper singlet excited state ($E_{S(\text{naph})} = 385 \text{ kJ mol}^{-1}$, Ref. [9,10,27]).

Triplet-sensitized reaction with acetophenone (Table 2, runs 5–7) in hexane led selectively to *ortho*-O ether **1** even at enhanced sensitizer concentration (4TBP/acetophenone = 1:5, run 7). The reaction proceeds probably from the upper triplet excited state ($E_{T(\text{acetoph})} = 310 \text{ kJ mol}^{-1}$) in comparison with benzophenone ($E_{T(\text{benzoph})} = 290 \text{ kJ mol}^{-1}$), as it was observed for 2TBP photoreactions [20].

The benzophenone-sensitized (Table 2, runs 8–9) reactions gave *ortho*-O ether **1** (33–34%) and moreover 2TBP (51–52%) and its *ortho*–*ortho* **3** (5–6%) and *ortho*–*para* **4** (9–10%) dimers. Compounds **3** and **4** are the consecutive photoreaction products of 2TBP (Scheme 2) and their ratio **3**:**4** = 0.56–0.6 is similar as for 2TBP sensitized photoreactions [20]. Triplet-sensitized photoreaction led to 2TBP as the major product (Table 2, runs 8–9). The conversion of 4TBP was greater (30–33%) in comparison with the other sensitizers.

The results of sensitized reactions again demonstrated the great effect of solvent polarity (Tables 1 and 2) on excited states of 4TBP. Phototransformations in the presence of singlet and triplet sensitizers confirmed that 4TBP conversion under UV and MW–UV radiation proceeded from the upper singlet state $[4\text{TBP}]^{S*}$ and from the normal or upper triplet state $[4\text{TBP}]^{T*}$. The quenching experiments (1,3-



Scheme 2. Consecutive photoreaction products **3** and **4**.

cyclohexadiene) [24] with 3TBP in cyclohexane gave no evidence of phenoxy radical formation via the first excited triplet state.

3.3. Mechanism of 4TBP phototransformation

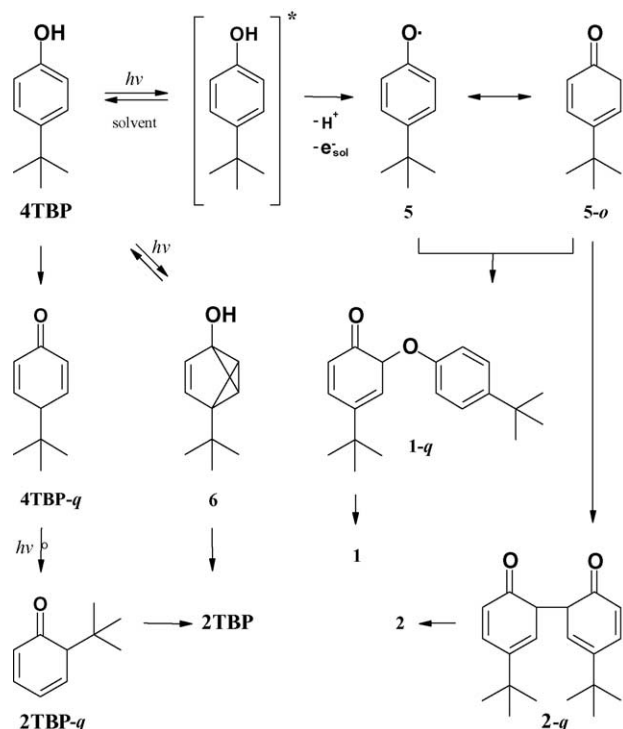
The direct phototransformation of 4TBP under UV and MW–UV radiation (Table 1, Scheme 1) led to C–O and C–C products: *ortho*-O ether **1**, *ortho*–*ortho* dimer **2** and 2TBP, their ratio depended upon solvent polarity and type of sensitizer. In non-polar solvents (hexane, heptane, toluene), 4TBP radiation afforded three products **1**, **2** and 2TBP where *ortho*–*ortho* dimer **2** is predominant over *ortho*-O ether **1**. In acetonitrile *ortho*–*ortho* dimer **2** was selectively formed, in 1,4-dioxane and in methanol no product formation was observed.

Influence of solvent polarity (acetone, hexane) on the relative products distribution of 4TBP photoreaction was also observed in the presence of sensitizers: acetone, naphthalene, acetophenone and benzophenone (Table 2). The acetone-sensitized reaction was found to give all three products: *ortho*-O ether **1**, *ortho*–*ortho* dimer **2** and 2TBP, where *ortho*-O ether **1** is predominant. In the presence of singlet sensitizer naphthalene the reaction of 4TBP in hexane gave mainly *ortho*-O ether **1** and 2TBP, whereas *ortho*–*ortho* dimer **2** was not found. Triplet-sensitized reaction with acetophenone in hexane led selectively to *ortho*-O ether **1**, while with benzophenone gave moreover 2TBP and its *ortho*–*ortho* **3** and *ortho*–*para* **4** dimers.

Solvents generally play an important role in the photo-physical and photochemical properties of the phenols. The deactivation of excited states in these compounds includes photochemical processes such as photodissociation or electron ejection accompanied by the production of a solvated electron depending on the solvent used. Extensive studies of phenols in various solvents [29] have shown that the photochemical cleavage of the O–H bond is the main process responsible for the variation in the behavior of the fluorescence quantum yield as a function of the excitation wavelength.

In the case of 2TBP irradiation [20], the *ortho*-O coupling diphenyl ether was not observed. Also 2-*tert*-butyl-4-methylphenol, 2,4- and 2,6-di-*tert*-butylphenol [14,30] afforded no products with oxygen bridge. These differences in 2-*tert*-butylphenols versus 4TBP reactivity appear to be related to steric effect of the *ortho*-substituent (*tert*-butyl group) rather than to its electronic effect (spin density distribution). The oxygen atom of 2TBP with the unpaired electron is hindered from C–O coupling by the neighboring bulky *tert*-butyl group in *ortho* position. When the *tert*-butyl was substituted by a methyl group, i.e. in 2,3-dimethylphenol [31] and 4-*tert*-butyl-2-methylphenol [14,32], the *ortho*-O coupling diphenyl ethers were observed.

The formation of rearranged product 2TBP is rationalized by a *valence photoisomerization* involving a benzvalene intermediate **6** (Scheme 3). This concurrent mechanism proceeds from singlet state [19]. However, there is another alter-



Scheme 3. Mechanism of 4TBP phototransformation.

native process including the ketone tautomer intermediates (Scheme 3). According to this mechanism, ketone tautomer **4TBP-q**, which is formed from the triplet state of 4TBP, is further transformed into 2TBP following the well-known photochemical processes for 2,5-cyclohexadienones [19]. It is probable that the 4TBP photoisomerization to 2TBP proceeds via the both mentioned mechanism involving the benzvalene **6** and ketone tautomer **4TBP-q** intermediates. The photoisomerization of 4TBP is result of ring carbon atom transpositions and it leads to a photostationary mixture. However, the 2TBP isomerization to 4TBP [20] was not observed (probably from thermodynamic reason), the similar results were indicated for photolysis of *o*-xylene [33].

The mechanism of the 4-*tert*-butyl phenoxy radical (**5**) formation is depicted in Scheme 3. By absorption of light ($h\nu$) under low excitation energy conditions (<0.5 mJ), the 4TBP molecule is promoted to a higher electronic state [4TBP]* [23] where, by solvation, a proton is splitted off to give phenoxy **5**. Under two photon excitation conditions (at laser power >0.5 mJ) [23] the radical **5** is assumed to originate via deprotonation of the phenol radical cation ArOH^+ and the solvated electron is immediately scavenged by the solvent [20]. The 4-*tert*-butyl phenoxy radical (**5**) and its cyclohexadienone keto tautomer **5-o** are stabilized by delocalization of their odd electron through the conjugated system and they can dimerize or recombine via a sandwich-like transition state [32] in dependence on conditions [18,34] of photoreaction (solvent polarity, sensibilization) to form tautomer *ortho*-O **1-q** and *ortho*–*ortho* **2-q** compounds of products **1** and **2**.

The stabilizing effect [23] of acetonitrile on phenoxy radical **5** (Table 1, runs 7–8) induced the formation of *ortho* radical **5-o** (Scheme 3), which after dimerization provided *ortho-ortho* dimer **2**. The rate of enolization of the cyclohexadienone dimer **2-q** would be expected to be greater in the more polar acetonitrile than in hexane [13]. Although it is difficult to explain the solvent effect in detail from the available experimental data, some of the pathways in Scheme 3 appear to be influenced by solvent polarity as was also observed in photochemical reactions of certain cyclohexadienones [19].

Therefore, it is necessary to consider whether the *ortho*-O ether **1** may rearrange to *ortho-ortho* dimer **2** by the consecutive photoreaction. However, in our case, the ratio of products $R_1 = (\textit{ortho-O}) \mathbf{1} / (\textit{ortho-ortho}) \mathbf{2}$ (Table 1, Fig. 1) was constant over all irradiation time.

It is known that diphenyl ethers are liable to rearrange via homolytic cleavage of C–O bond in the singlet excited state to generate radical pair intermediate involving phenyl and phenoxy radicals that may undergo rapid recombination to give rearrangement products (2- and 4-phenylphenol) in addition to diffusion products (phenol and benzene) [22]. Cross-coupling experiments demonstrated that the formation of 2- and 4-phenylphenol was an intramolecular process. The photolysis of 2-hydroxydiphenyl ether (C₆H₅–O–C₆H₄–OH) [34] in water produced the phenyl (C₆H₅) and 2-hydroxyphenoxy ($\bullet\text{O}-\text{C}_6\text{H}_4-\text{OH}$) radicals through phenyl-aryloxy bond cleavage. The radical recombination is highly selective and nonrandom with coupling in positions *ortho* or *para* to the cleaved oxygen. Isolated products were catechol, biphenyl-2,3-diol and biphenyl-3,4-diol. The irradiation of 4',5-dimethyl-2-hydroxydiphenyl ether afforded only 4-methylcatechol [34]. In our case, no derivative of catechol as a product of phenyl-aryloxy bond cleavage of **1** was observed. The rearrangement of *ortho*-O ether **1** to *ortho-ortho* dimer **2** under our conditions did not proceed.

Strong differences in the effect of UV or MW–UV radiation on the relative products distribution of 4TBP photolysis were not observed, only the slight indication for hexane as solvent was quoted. Therefore, it can be concluded that MW radiation (in the microwave photochemistry area) mainly acted on generation of effective UV radiation from the electrodeless discharge lamp. On the other hand, the 4TBP photoreaction can be straight driven by choice of suitable solvent or sensitizer on purpose to selectively prepare only one product, i.e. *ortho-ortho* dimer **2** formed in acetonitrile and triplet-sensitized reaction with acetophenone in hexane led to *ortho*-O ether **1**.

Acknowledgements

This work was supported by the Grant Agency of the Czech Republic (Grant No. 203/02/0879) and the project AS CR No. K4040110.**

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