

Microwave photochemistry

II. Photochemistry of 2-*tert*-butylphenol

Vladimír Církva*, Jana Kurfürstová, Jindřich Karban, Milan Hájek

Institute of Chemical Process Fundamentals, Academy of Sciences of the Czech Republic, Rozvojová 135, 16502 Praha 6, Czech Republic

Received 1 March 2004; received in revised form 26 May 2004; accepted 27 May 2004

Available online 23 July 2004

Abstract

Influence of UV and combined MW–UV irradiation on 2-*tert*-butylphenol (2TBP) 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 combination MW–UV gave three C–C dimers: 3,3'-di-*tert*-butylbiphenyl-2,2'-diol (**1**) (*ortho–ortho*), 3,3'-di-*tert*-butylbiphenyl-2,4'-diol (**2**) (*ortho–para*) a 3,3'-di-*tert*-butylbiphenyl-4,4'-diol (**3**) (*para–para*). Their ratio depends upon the nature of solvents and sensitizers used. In non-polar solvents (hexane, heptane, benzene, toluene), direct 2TBP radiation led to the formation of two products **1** and **2** where *ortho–para* **2** is predominant over *ortho–ortho* dimer **1**. Irradiation in dipolar aprotic solvent 1,4-dioxane led only to *ortho–ortho* **1** and in case of acetonitrile only to *ortho–para* dimer **2**. In polar solvents (acetic acid, water, methanol/water = 1:1 v/v), it led to the formation of all three products. In methanol, the reaction did not proceed. Influence of solvent polarity (hexane, acetonitrile) to relative product distribution of 2TBP photoreaction was also observed in the presence of sensitizers: acetophenone, benzophenone, naphthalene, acridine and anthracene. Reaction in hexane gave *ortho–ortho* **1** and *ortho–para* **2** dimers with all tested sensitizers. The acridine-sensitized reaction in acetonitrile was found to give *ortho–para* **2** and a greater amount of *para–para* **3** dimer. Singlet-sensitized reaction (naphthalene, anthracene) in acetonitrile led to *ortho–para* dimer **2**. Nonsensitized as well as singlet-sensitized reaction of 2TBP proceeded from singlet state situated under singlet state energy of anthracene (320 kJ mol⁻¹). Triplet state of 2TBP was found to be under triplet state of benzophenone (290 kJ mol⁻¹).

Keywords: Microwave photochemistry; Electrodeless discharge lamp; 2-*tert*-Butylphenol

1. Introduction

Microwave photochemistry [1] is one of the interesting field of modern microwave chemistry. In the past five years over 30 papers dealing with combination of the microwave and ultraviolet irradiation have been published [2–6]. The fundamental principles of microwave photochemistry have been described by us [1–4]. Such a combination might have a synergic thermal (superheating) and non-thermal (inter-system crossing in radical recombination) microwave effect on the course of photoreaction [1].

The transformation of 2-*tert*-butylphenol (2TBP) under microwave conditions has been studied in the liquid phase (polar and non-polar solvents) on a heterogeneous catalyst (Montmorillonite KSF) [7,8]. The process includes dealkylation, isomerization and transalkylation reactions.

Photochemistry of 2TBP has been investigated in view of exchanges of the excited states, their overall lifetimes and influence of stability by solvents of different polarity [9–11]. These photophysical papers have been published on generation and kinetics of phenoxy radicals and on deactivation channels of the first excited singlet state. The relaxation of the first excited level S₁ takes place extremely fast (10⁹ s⁻¹) and proceeds exclusively by internal conversion [9].

The photochemical transformation of 2TBP in the presence of acridine as sensitizer in benzene and acetonitrile has been investigated by Okada and Okubo [12]. *Para–para* dimer of phenol and biacridane were identified as products. Direct and sensitized irradiation of 2,6-di-*tert*-butylphenol and its 4-substituted derivatives gave the rearranged isomeric phenols accompanied by a de-*tert*-butylated product [13]. The reaction occurred through a ketone tautomer of the parent phenols.

The photooxidation of *o*-, *m*- and *p*-cresols [14] in water in the presence of oxygen yielded the C–C or C–O dimers and products of hydroxylation. 2,6-Dimethylphenol in aerated

* Corresponding author.

E-mail address: cirkva@icpf.cas.cz (V. Církva).

aqueous solution gave 2,6-dimethylbenzoquinone and the *para-para* coupling dimer as major products [15,16].

In the present study we describe the influence of UV and combined MW–UV irradiation on 2TBP 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 in the modified MW oven (Whirlpool M435, 900 W) operating at 2.45 GHz frequency and described elsewhere [4]. Electrodeless discharge lamps (EDL) were manufactured in Teslamp (Prague, Czech Republic). The lamp was made of a 14 mm quartz tubing of the 40 mm length, filled with mercury and argon, and sealed under 2.7 kPa vacuum [5].

Classical immersion-well photoreactor (300 ml) contained a medium-pressure UV lamp (Teslamp, RVK 125) in a water-cooled double jacket (quartz and Simax® glass) and Dimroth condenser.

GC was performed on an HP 5890 instrument with HP-5 column (i.d. 0.2 mm, $l = 25$ m), injector (250 °C), FID detector (250 °C) and nitrogen as a carrier gas. GC/MS analysis was accomplished on an HP 6890 instrument with mass detector HP 5973 (70 eV), DB-5ms column (i.d. 0.25 mm, $l = 30$ m) and helium as a carrier gas.

^1H and ^{13}C NMR spectra were recorded on Varian Mercury VX300 instrument using tetramethylsilane as the internal standard. Chemical shifts are quoted in ppm (singlet; broad singlet; d, doublet; t, triplet; m, multiplet), coupling constants J in Hz, solvent CDCl_3 .

2.2. Chemicals

Acetophenone (99%), acridine (97%), benzaldehyde (98%), biphenyl-2,2'-diol (99%), 2-*tert*-butylphenol (99%), naphthalene (98%) (all from Sigma-Aldrich); aluminum chloride (99%), benzophenone (99%), bromine (99%), di-*tert*-butyl peroxide (95%) (all from Fluka); aluminum oxide (Brockmann II, neutral), anthracene (p.a.), fluorescein (p.a.), hydrochloric acid (p.a.), Raney nickel, sodium hydroxide (p.a.), zinc (powder, 98%) (all from Lachema, Brno) were used as received. Solvents (acetic acid, acetone, acetonitrile, benzene, chloroform, dichloromethane, 1,4-dioxane, diethyl ether, heptane, hexane, methanol, toluene) were purified by distillation (all p.a., Lachema, Brno). The quality of all solvents was verified by the UV–vis spectrophotometer (Helios γ , Thermo Electron, USA) and GC.

2.3. Photochemical experiments

2TBP (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. Temperature of mixture was maintained at reflux by the external oil bath. If required, the solution was purged with argon or air for 0.5 h prior to and during photolysis. The results of measurements are listed in Tables 1 and 2.

2.4. Microwave photochemical experiments

2TBP (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 2) was irradiated for 2 h by an electrodeless discharge lamp placed into the reaction solution in the MW field [4]. Temperature of mixture was maintained at reflux by the convective heating of EDL. If required, the solution was purged with argon or air for 0.5 h prior to and during photolysis. The results of measurements are listed in Tables 1 and 2.

2.5. Photoproduct identification and analysis

The photoproduct concentrations and conversions were determined by GC and GC/MS methods. The identification of the products was based on the comparison of their retention times or mass spectra with those obtained from authentic samples. All the mentioned results are summarized in Tables 1 and 2.

2.5.1. Photoproducts 1 and 2 from 2TBP in hexane under MW–UV irradiation (Table 1, run 1)

The crude photoreaction mixture was steam distilled and concentrated under reduced pressure (80 °C, 666 Pa). Chromatography of yellow oil on 1.4 cm \times 60 cm alumina column eluted with 0.5% *tert*-butanol in dichloromethane-hexane (1:1 v/v) mixture gave 84 mg (7%) of 3,3'-di-*tert*-butylbiphenyl-2,2'-diol (**1**) as viscous oil and 95 mg (8%) of 3,3'-di-*tert*-butylbiphenyl-2,4'-diol (**2**) as viscous oil.

The spectral characteristics of **1** were as follows: ^1H NMR (CDCl_3) δ : 1.44 (s, 18H, CH_3); 5.27 (bs, 2H, OH); 6.94 (dd, 2H, arom 5-H, $^3J = 7.7$, $^3J = 7.3$); 7.07 (dd, 2H, arom 4-H, $^3J = 7.3$, $^4J = 1.8$); 7.34 (dd, 2H, arom 6-H, $^3J = 7.7$, $^4J = 1.8$) ppm. ^{13}C NMR (CDCl_3) δ : 29.6 (s, 6C, CH_3); 35.1 (s, 2C, C); 120.5 (s, 2C, arom 5-C); 122.4 (s, 2C, arom 4-C); 127.7 (s, 2C, arom 6-C); 128.6 (s, 2C, arom 1-C); 137.1 (s, 2C, arom 3-C); 152.1 (s, 2C, arom 2-C) ppm. MS m/z (abund./%): 299 (14), 298 (65, $\text{M}^{+\bullet}$), 284 (12), 283 (59, $\text{M}-\text{CH}_3^+$), 228 (17), 227 (100), 199 (5), 165 (6), 134 (8), 120 (9), 106 (22), 105 (5), 57 (31, $t\text{-Bu}^+$), 41 (5).

The spectral characteristics of **2** were as follows: ^1H NMR (CDCl_3) δ : 1.43 a 1.44 ($2 \times$ s, 18H, CH_3); 5.23 a 5.49 ($2 \times$ bs, 2H, OH); 6.77 (d, 1H, arom 5'-H, $^3J = 8.4$); 6.87 (t,

Table 1
Transformation of 2TBP by UV and combined MW–UV radiation in solvents with different polarity^a

Run	Solvent	Type of radiation	Relative products distribution (%) ^b			<i>R</i> ₁ (2)/(1)	Conversion 2TBP (%)
			1	2	3		
1	Hexane	MW–UV	45	55	0	1.2	27
2		UV	36	64	0	1.8	22
3		MW–UV ^c	43	57	0	1.3	32
4		MW–UV ^d	57	43	0	0.8	2
5		UV ^e	25	75	0	3.0	16
6		UV ^f	8	12	80	1.5	20
7		MW–UV ^g	35	65	0	1.9	23
8		MW–UV ^h	36	64	0	1.8	27
9		UV ^h	35	65	0	1.9	26
10	Heptane	MW–UV	45	55	0	1.2	36
11		UV	45	55	0	1.2	36
12	Benzene	MW–UV	50	50	0	1.0	16
13	Toluene	MW–UV	44	56	0	1.3	18
14	1,4-Dioxane	MW–UV	100	0	0	–	2
15		UV	100	0	0	–	4
16	Acetonitrile	MW–UV	0	100	0	–	10
17		UV	0	100	0	–	7
18	Methanol	MW–UV	0	0	0	–	0
19		UV	0	0	0	–	0
20	Acetic acid	MW–UV	12	73	15	6.1	7
21	Water–methanol ⁱ	MW–UV	12	64	24	5.3	2
22	Water	MW–UV	11	62	27	5.6	8
23		UV	13	70	17	5.4	2

^a 2TBP concentration 0.04 mol l⁻¹; irradiation time 2 h at reflux. MW–UV: experiments with 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 ±5%.

^c 2TBP concentration 0.08 mol l⁻¹.

^d The molar ratio of 2TBP/hexane = 1:1; irradiation time 6 h.

^e At room temperature.

^f At room temperature; Pyrex.

^g Reaction mixture was bubbled with argon.

^h Reaction mixture was bubbled with air.

ⁱ Ratio water/methanol = 1:1 v/v.

1H, arom 5-H, ³J = 7.5); 7.04 (dd, 1H, arom 4-H, ³J = 7.5, ⁴J = 1.8); 7.12 (dd, 1H, arom 6'-H, ³J = 8.4, ⁴J = 1.8); 7.25 (dd, 1H, arom 6-H, ³J = 7.5, ⁴J = 1.8); 7.29 (d, 1H, arom 2'-H, ⁴J = 1.8) ppm. ¹³C NMR (CDCl₃) δ: 29.6 a 29.7 (2 × s, 6C, CH₃); 34.8 a 35.0 (2 × s, 2C, C); 117.2 (s, 1C, arom 5'-C); 119.5 (s, 1C, arom 5-C); 126.0 (s, 1C, arom 2'-C); 127.8 (s, 1C, arom 4-C); 127.9 (s, 1C, arom 6'-C); 128.5 (s, 1C, arom 6-C); 128.8 (s, 1C, arom 1-C); 128.9 (s, 1C, arom 1'-C); 135.8 (s, 1C, arom 3'-C); 137.3 (s, 1C, arom 3-C); 151.1 (s, 1C, arom 2-C); 154.1 (s, 1C, arom 4'-C) ppm. MS *m/z* (abund. %): 299 (22), 298 (100, M^{•+}), 284 (11), 283 (51, M-CH₃⁺), 255 (5), 228 (11), 227 (66), 213 (5), 165 (6), 134 (11), 120 (11), 106 (26), 105 (6), 57 (43, *t*-Bu⁺).

2.5.2. Dealkylation of 3,3'-di-*tert*-butylbiphenyl-2,2'-diol (1)

The mixture of 3,3'-di-*tert*-butylbiphenyl-2,2'-diol (1) (30 mg, 0.1 mmol), aluminum chloride (13 mg, 0.1 mmol) and benzene (1 ml) was stirred at room temperature overnight, worked up with ice and extracted with di-

ethyl ether [13]. Concentration of the extracts in vacuo afforded a yellow oil of biphenyl-2,2'-diol. The structure was confirmed by mass spectra (NIST database). MS *m/z* (abund. %): 187 (14), 186 (100, M^{•+}), 185 (27), 169 (8), 158 (9), 157 (24), 139 (6), 131 (16), 129 (10), 128 (16), 115 (8), 102 (3), 89 (2), 77 (6), 63 (4).

2.5.3. Preparation of 3,3'-di-*tert*-butylbiphenyl-2,4'-diol (2) (preparation of standard)

The mixture of 2TBP (15 g, 0.1 mol) and di-*tert*-butyl peroxide (2.9 g, 0.02 mol) was heated for 23 h at 140 °C [17]. The excess of 2TBP was removed by steam distillation, GC analysis shown 68% (1), 27% (2) and 5% (3) at 18% conversion of 2TBP. Chromatography of yellow oil on 3 cm × 100 cm alumina column eluted with dichloromethane-hexane (1:5, 1000 ml) mixture, (2:5, 700 ml) mixture, dichloromethane (700 ml) and acetone (700 ml) gave 0.84 g (5.6%) of 1, 0.33 g (2.2%) of 2 and 60 mg (0.4%) of 3, all as viscous oils.

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

Run	Solvent	Sensitizer	Type of radiation	Relative products distribution (%) ^b			R_2 (2)/(1)	Conversion 2TBP (%)	
				1	2	3			
1	Hexane	Acetophenone	MW–UV	44	56	0	1.3	27	
2			UV	43	57	0	1.3	32	
3			MW–UV ^c	46	54	0	1.2	21	
4			MW–UV ^d	40	60	0	1.5	32	
5		Benzophenone	MW–UV	40	60	0	1.5	38	
6			UV	46	54	0	1.2	34	
7		Naphthalene	MW–UV	32	68	0	2.1	18	
8			UV	27	73	0	2.7	16	
9		Acridine	MW–UV	13	87	0	6.7	12	
10			UV	18	82	0	4.6	9	
11			MW–UV	38	62	0	1.6	18	
12	Acetonitrile	Acetophenone	MW–UV	55	29	16	0.5	24	
13			Naphthalene	MW–UV	0	100	0	–	5
14			Acridine	MW–UV	0	45	55	–	22
15			UV	0	45	55	–	23	
16			UV ^e	0	34	66	–	17	
17		Anthracene	MW–UV	0	100	0	–	4	

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

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

^c Reaction mixture was bubbled with argon.

^d The molar ratio of 2TBP/acetophenone = 1:5.

^e 2TBP concentration 0.02 mol l^{-1} ; irradiation time 6 h at room temperature; Pyrex [12].

2.5.4. Preparation of 3,3'-di-tert-butylbiphenyl-4,4'-diol (3) (preparation of standard)

The mixture of 3,3'-dibromo-5,5'-di-tert-butylbiphenyl-4,4'-diol (**5**) (1.62 g, 3.6 mmol), 8.1 ml 95% ethanol, 5 g Ra–Ni and 48.6 ml 10% solution of sodium hydroxide was stirred in flask (100 ml) at reflux for 90 min. The Ra–Ni was filtered and washed with 10% sodium hydroxide and followed by benzene. The cooled reaction mixture was poured into 40 ml of concentrated hydrochloric acid, extracted with benzene and dried over anhydrous sodium sulfate. The solvent was removed and concentration in vacuo afforded a yellow solid. Recrystallization from petroleum ether yielded 1.18 g (96,7%) of 3,3'-di-tert-butylbiphenyl-4,4'-diol (**3**) as colorless needles, mp 179–180 °C (lit. [18]: 181–183.5 °C).

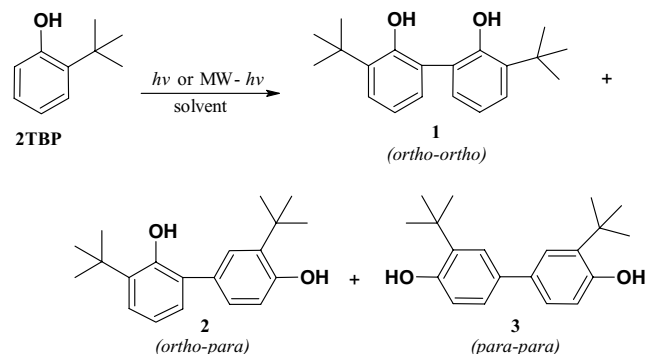
The spectral characteristics of **3** were as follows: ¹H NMR (CDCl₃, 300 MHz) δ : 1.45 (s, 18H, CH₃); 4.72 (bs, 2H, OH); 6.71 (d, 2H, arom 5-H, ³J = 8.1); 7.23 (dd, 2H, arom 6-H, ³J = 8.1, ⁴J = 2.3); 7.43 (d, 2H, arom 2-H, ⁴J = 2.3) ppm. ¹³C NMR (CDCl₃) δ : 29.6 (s, 6C, CH₃); 34.6 (s, 2C, C); 116.8 (s, 2C, arom 5-C); 125.3 (s, 2C, arom 2-C); 125.9 (s, 2C, arom 6-C); 134.1 (s, 2C, arom 1-C); 136.2 (s, 2C, arom 3-C); 153.2 (s, 2C, arom 4-C) ppm. MS m/z (abund./%): 299 (23), 298 (100, M^{•+}), 284 (16), 283 (72, M–CH₃⁺), 255 (20), 134 (7), 120 (6), 106 (19), 57 (10, *t*-Bu⁺).

3. Results and discussion

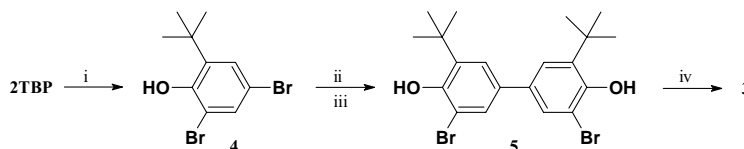
The UV and combined MW–UV irradiation of 2TBP gave three C–C dimers (Scheme 1): 3,3'-di-tert-butylbiphenyl-

2,2'-diol (**1**) (*ortho–ortho*), 3,3'-di-tert-butylbiphenyl-2,4'-diol (**2**) (*ortho–para*) and 3,3'-di-tert-butylbiphenyl-4,4'-diol (**3**) (*para–para*).

The photoproducts **1** and **2** were isolated from the reaction mixture by column chromatography on alumina (Section 2.5.1), and the structures were confirmed by NMR and MS spectra. Structure of *ortho–ortho* dimer **1** was confirmed also by dealkylation reaction with aluminum chloride [13] (Section 2.5.2) to afford biphenyl-2,2'-diol (identified by comparison with NIST spectra database). The *ortho–para* product **2** was prepared by independent reaction of 2TBP with di-tert-butyl peroxide [17] (Section 2.5.3). The *para–para* product **3** was prepared using four-step procedure (Scheme 2). First step is bromination (Br₂) of 2-tert-butylphenol [19] in methanol at room temperature affording 2,4-dibromo-6-tert-butylphenol (**4**). In the fol-



Scheme 1. Photoreaction products of 2TBP.



Scheme 2. Preparation of photoproduct **3** (as standard) (i) Br₂, MeOH, rt; (ii) 80 °C, 10% aq. NaOH, 15 min; (iii) Zn, acetic acid; (iv) Ra–Ni.

lowing step is **4** dissolved in 10% sodium hydroxide and heated at 80 °C for 15 min to give the brown complex of **4** [20]. Decomposition of complex by Zn in acetic acid affords 3,3'-dibromo-5,5'-di-*tert*-butylbiphenyl-4,4'-diol (**5**) [20]. The last step is debromination of diol **5** by Ra–Ni in ethanol [21] yielding diol **3**.

3.1. Influence of solvent polarity

It is known that, by absorption of UV light, the molecule of 2TBP is promoted to a higher electronic state. The initially excited molecule is obviously energetically unstable and will find some way of losing its excitation energy by returning to the ground state (photophysics, radiative and nonradiative processes) or to rearrange and exchange its chemical integrity (photochemistry) [22]. The molecule in the excited state is also influenced by the surrounding solvent from the two angles: (i) the interaction of hydrogen bonds of solvent and solute molecules, and (ii) the effect of solvent polarity (dielectric constant) [9,23–26].

Transformation of 2TBP by UV and combined MW–UV radiation was investigated in the presence of solvents (Table 1) with different polarity. The reaction mixture of 2TBP (0.04 mol l⁻¹) in various solvents was irradiated for 2 h at the reflux temperature. The results of individual experiments (according to GC analysis, runs 1–23) were compared with respect to relative products distribution and to ratio of products $R_1 = (\textit{ortho-para}) \mathbf{2}/(\textit{ortho-ortho}) \mathbf{1}$.

In non-polar solvents (hexane, heptane, toluene, benzene), direct 2TBP radiation (Scheme 1) led to the formation of two products **1** and **2** where *ortho-para* **2** was mildly predominant over *ortho-ortho* dimer **1** (Table 1, runs 1–13). The slight effect of UV and combined MW–UV radiation was observed only for hexane (Table 1, runs 1–2, $R_1 = 1.2$ versus 1.8). Conversions of 2TBP after 2 h irradiation in hexane and heptane ranged from 22 to 36% (Table 1, runs 1–2, 10–11). The combined MW–UV irradiation of 2TBP was carried out also in benzene and toluene (Table 1, runs 12–13). Relative product distribution was comparable to that for hexane and heptane. Conversions of 2TBP were only 16–18% owing to high efficiency of aromatic ring to absorb UV radiation in the region 230–260 nm [27]. Also the light performance of electrodeless lamp in benzene 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.

The effect of 2TBP concentration on relative products distribution was investigated in hexane under combined MW–UV radiation (Table 1). The reaction mixture was irradiated either for 2 h at double 2TBP concentration (0.08 mol l⁻¹, run 3) or for 6 h at the molar ratio 2TBP/hexane = 1:1 (run 4). The double concentration increase did not influence the ratio of products **1** and **2** (run 3). However, it was observed that reaction rate at ratio 2TBP/hexane = 1:1 was decreased (conversion 2%, run 4) and ratio $R_1 = 0.8$ indicated mild preference of *ortho-ortho* dimer **1**. This selectivity change in reaction products **1** and **2** can be explained by the increased viscosity of mixture when the phenoxy radical **6** (Scheme 4) must dimerize to product **1** very fastly.

The temperature effect on 2TBP irradiation was investigated in hexane under UV radiation (Table 1, run 5). The reaction mixture was irradiated at room temperature for 2 h when it was observed that the content of *ortho-para* dimer **2** increased (75%) and conversion of 2TBP decreased (16%), in comparison with the same experiment at the reflux temperature (Table 1, run 2, 22%). The temperature effects were therefore studied in non-polar solvents with increasing boiling point (hexane, heptane). Relative products distributions **1** and **2** were comparable and independent of temperature. Conversion of 2TBP increased with reflux temperature, i.e. for heptane 36% (runs 10,11) versus hexane 27% and 22% (runs 1, 2).

The effect of irradiation wavelength on 2TBP phototransformation was investigated in hexane under UV radiation with glass (Pyrex) filter (Table 1, run 6). The reaction mixture was irradiated at room temperature for 2 h and three photoproducts were found, *ortho-ortho* dimer **1** (8%), *ortho-para* dimer **2** (12%) and *para-para* dimer **3** (80%). The conversion of 2TBP (20%) was comparable to that without filter (Table 1, runs 2,5). The formation of *para-para* dimer **3** as major photoproduct was observed only in hexane over a Pyrex filter. The reason for this result is the influence of long wavelength irradiation on stability of phenoxy radical **6** and its cyclohexa-2,5-dienone keto tautomers (Scheme 4, **6-o**, **6-p**).

The effect of oxygen and argon on relative product distribution of 2TBP reaction was investigated in hexane (Table 1, runs 7–9) by bubbling dry air or argon through the irradiated solution. Molecular oxygen is an effective quencher of triplet excited states ($E_T = 96 \text{ kJ mol}^{-1}$) [22]. The presence of oxygen in our experiments (runs

8–9) had no influence on the photochemical reaction, a decrease of 2TBP conversion was not observed and the relative products distribution was comparable. Therefore, it is possible to assume that the direct 2TBP phototransformation to dimers **1** and **2** proceeds from the excited singlet state.

Irradiation of 2TBP in dipolar aprotic solvents (1,4-dioxane, acetonitrile) led selectively only to one specific product (Table 1, runs 14–17), in dioxane *ortho–ortho* dimer **1** and in acetonitrile *ortho–para* dimer **2** was observed. The high product selectivity was probably affected by viscosity of solvents and their ability to stabilize free radicals (by electron delocalization). The viscosity of 1,4-dioxane (1.204 cP, [27]) was 3.5 times higher than for acetonitrile (0.342 cP) and therefore photoreaction of phenoxyl radical **6** (Scheme 4) led in a viscous solvent directly to *ortho–ortho* dimer **1** (runs 14–15). However, the stabilizing effect of acetonitrile on radical **6** induces the formation of *para* radical **6-p** (Scheme 4) which after recombination provides *ortho–para* dimer **2** (runs 16–17). The effect of UV and combined MW–UV radiation on relative product distribution was not observed.

Similar behaviour was also observed in photorearrangement of diphenyl ether [27]. The results indicated excitation to the singlet state and dissociation to a radical pair intermediate involving phenoxyl and phenyl radicals. Intramolecular recombination of these radicals gives rearrangement products (2- and 4-phenylphenol), and escape gives diffusion products (phenol, benzene). The combined yields of rearrangement products increased with an increase of solvent viscosity whereas the yields of diffusion products decreased.

In polar solvents (acetic acid, water, methanol/water = 1:1 v/v), direct 2TBP irradiation (Scheme 1) led to the formation of all three products **1–3** where *ortho–para* **2** (62–73%) is predominant over *ortho–ortho* **1** (11–13%) and *para–para* **3** (15–27%) (Table 1, runs 20–23). However, conversion of 2TBP was very low (2–8%). In methanol, reaction did not proceed (runs 18–19). The relative product distribution was dependent on solvent polarity. Under protic conditions, hydrogen bonds are formed with the hydroxyl group of the phenols [9]. 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 prolongation indicates the higher stability of the S_1 state in the presence of hydrogen bonds compared to the nonpolar or aprotic situation (fluorescence lifetimes for 2TBP are $\tau_f = 2.2$ ns in water and $\tau_f = 0.46$ ns in hexane) [9]. The phenoxyl radical **6** has then some time to form *para* radical **6-p** (Scheme 4). In this way is possible to explain the low content of *ortho–ortho* product **1** (11–13%), the relative great distribution of *ortho–para* product **2** (62–73%) and the occurrence of *para–para* product **3** (15–27%) in polar solvents (Table 1, runs 20–23).

3.2. Effect of sensitizers

Influence of solvent polarity (hexane, acetonitrile) to relative product distribution of 2TBP reaction was also investigated in the presence of sensitizers: acetophenone, benzophenone, naphthalene, acridine and anthracene. The absorption bands of 2TBP in tested solvents ($\epsilon_{269} = 20001 \text{ mol}^{-1} \text{ cm}^{-1}$) overlapped absorption bands of used sensitizers [28].

Reaction in hexane gave *ortho–ortho* **1** and *ortho–para* **2** dimers with all tested sensitizers (Table 2, runs 1–11). In case of *acetophenone* (runs 1–4), the ratio R_2 was comparable with R_1 for nonsensitized photoreaction (Table 1, runs 1, 3). The presence of argon (Table 2, run 3) and the increased amount of sensitizer (2TBP/acetophenone = 1:5, run 4) had no influence on the relative products distribution. The *benzophenone*-sensitized (runs 5–6) reactions led to the similar ratio of products, however conversion of 2TBP was greater (38%). The presence of tetraphenylethane-1,2-diol (the photoreduction product) was not observed.

The triplet energy for benzophenone is 290 kJ mol^{-1} , for 2,6-di-*tert*-butylphenol (DTBP) with similar structure as 2TBP is 280 kJ mol^{-1} [13]. This value is relatively low comparing with triplet energies of phenol (346 kJ mol^{-1}) and 4-methylphenol (335 kJ mol^{-1}) [29] probably due to the lowering effect of electron-donating group. From this information is possible to suppose that triplet energy of 2TBP occurs under triplet state of benzophenone and above triplet state of DTBP, i.e. between 290 and 280 kJ mol^{-1} .

Irradiation of 2TBP in hexane with *naphthalene* as sensitizer led to the drop in conversion to 16% and to the increase in dimer **2** content to 73% (Table 2, runs 7–8). The acridine sensibilization (runs 9–10) enhanced the amount of **2** even to 87%. In case of *anthracene* (run 11) the relative products distribution was the same as for benzophenone.

The stability of excited states is strongly affected by solvent polarity, therefore some experiments were performed in acetonitrile (Table 2, runs 12–17). 2TBP was then irradiated in the presence of acetophenone, naphthalene, anthracene and acridine.

The *acetophenone*-sensitized reaction in acetonitrile led to the formation of all three products: *ortho–ortho* **1** (55%), *ortho–para* **2** (29%) and *para–para* **3** (16%) (Table 2, run 12). The greater content of dimer **1** results due to energy transfer from high triplet state of acetophenone $[2\text{TBP}]^{T*}$ ($E_T = 310 \text{ kJ mol}^{-1}$). Deactivation proceeds with higher rate and the originating radicals **6-o** (Scheme 4) are partly stabilized by acetonitrile.

Irradiation of 2TBP in acetonitrile with naphthalene and anthracene (Table 2, runs 13, 17) as sensitizers led only to *ortho–para* dimer **2**, similar to nonsensitized reaction (Table 1, runs 16, 17). Conversion of 2TBP dropped to 4% (runs 7, 8, 11). Naphthalene and anthracene acted as singlet sensitizers (energy $E_{S(\text{naph})} = 385 \text{ kJ mol}^{-1}$, $E_{S(\text{anth})} = 320 \text{ kJ mol}^{-1}$) and therefore, the reaction of 2TBP pro-

ceeded from the singlet state situated under singlet state energy of anthracene, i.e. 320 kJ mol^{-1} .

The *acridine*-sensitized reaction in acetonitrile under UV and combined MW–UV radiation was found to give *ortho*–*para* **2** (45%) and greater amount of *para*–*para* **3** (55%) dimers (Table 2, runs 14–15). Major product **3** resulted from the electron donor effect of triplet sensitizer in photoelectron transfer reaction and CIDEP study established the path of hydrogen abstraction by the triplet acridine [12]. The stabilizing effect of solvent (acetonitrile versus hexane) on phenoxyl radical **6** was also considered. *Acridine*-sensitized reaction of 2TBP has been studied [12] in various solvents. The *para*–*para* dimer **3** (47% in acetonitrile, 16% in benzene) and biacridane were only isolated products. The reaction mixture under the same conditions (Pyrex filter, 6 h) was therefore irradiated (Table 2, run 16) and two photoproduct were obtained: *ortho*–*para* **2** (34%) and *para*–*para* **3** (66%) dimers, similar to runs 14 and 15. The presence of photoproduct **2** gave reasons for reaction path through recombination of phenoxyl radical **6** to **2-q** (Scheme 4). The results of sensitized reactions again demonstrated the great effect of solvent polarity (Table 2, hexane versus acetonitrile) on excited states of 2TBP. Phototransformations in the presence of singlet and triplet sensitizers confirmed that 2TBP conversion under UV and combined MW–UV radiation proceeded from singlet state $[2\text{TBP}]^{S*}$ and triplet state $[2\text{TBP}]^{T*}$.

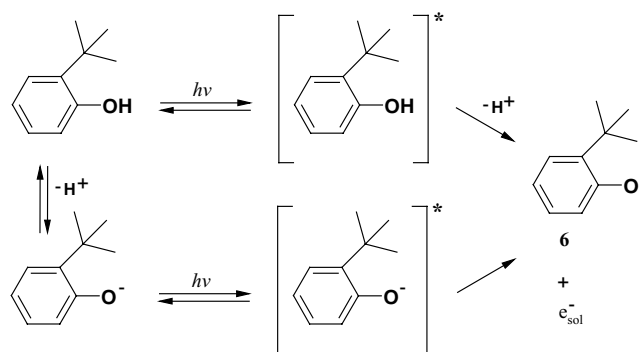
3.3. Phototransformation of 2TBP

Phototransformation of 2TBP under UV and combined MW–UV radiation led to three C–C dimers: *ortho*–*ortho* **1**, *ortho*–*para* **2** and *para*–*para* **3**, their ratio depended upon solvent polarity and type of sensitizer. In non-polar solvents, 2TBP radiation afforded two products **1** and **2** (Table 1). The relative products distribution was changed with increased solvent polarity by stabilization of phenoxyl radical **6** (acetonitrile, *ortho*–*para* product **2**) or by hydrogen bond formation (water, *para*–*para* product **3**).

The presence of oxygen (Table 1, runs 8–9) had no influence on the photochemical reaction, therefore it was possible to presuppose that the direct 2TBP phototransformation to dimers **1** and **2** proceeds from the excited singlet state $[2\text{TBP}]^{S*}$.

Irradiation of 2TBP in the presence of singlet (naphthalene, anthracene) and triplet sensitizers (acetophenone, benzophenone, acridine) in hexane (Table 2, runs 1–6, 9–10) led to two product **1** and **2** from singlet $[2\text{TBP}]^{S*}$ or triplet state $[2\text{TBP}]^{T*}$. Formation of product **3** in the presence of triplet sensitizers (acetophenone, acridine) (Table 2, runs 12, 14–16) was explained by stabilizing effect of acetonitrile to phenoxyl radical **6**.

The mechanism of the 2-*tert*-butyl phenoxyl radical (**6**) formation is depicted in Scheme 3 [9,14]. By absorption of light ($h\nu$), the 2TBP molecule is promoted to a higher

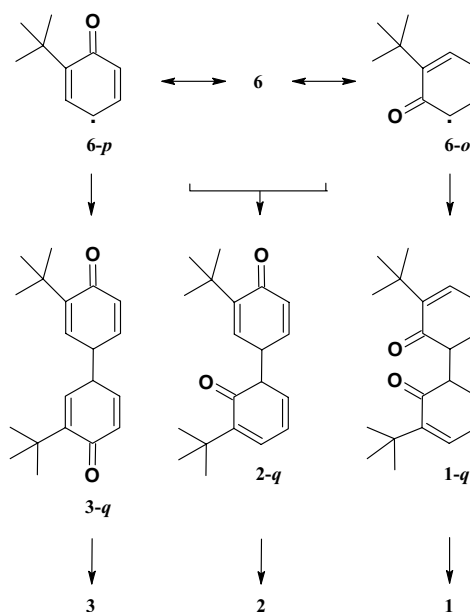


Scheme 3. Formation of 2-*tert*-butyl phenoxyl radical (**6**).

electronic state $[2\text{TBP}]^*$ where, by solvation a proton, is splitted off to give phenoxyl radical **6** and solvated electron (e^-_{sol}). At the same time, the 2TBP molecule can be solvated in ground state and the excited phenolate $[2\text{TBP}^-]^*$ forms again phenoxyl radical **6**.

The 2-*tert*-butyl phenoxyl radical (**6**) and its cyclohexadienone keto tautomers (Scheme 4, **6-o**, **6-p**) can dimerize or recombine in dependence [14–16,30] on conditions of reaction (solvent polarity, sensibilization) to form *ortho*–*ortho* **1-q**, *ortho*–*para* **2-q** and *para*–*para* **3-q** tautomer dimers of products **1–3**.

Strong differences in the effect of UV and combined MW–UV radiation on relative product distribution of 2TBP photolysis were not observed. 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.



Scheme 4. Phototransformation of 2TBP.

Acknowledgements

This work was supported by the Grant Agency of the Czech Republic (Grant No. 203/02/0879).

References

- [1] P. Klán, V. Církva, Microwave Photochemistry, in: A. Loupy (Ed.), *Microwaves in Organic Synthesis*, Wiley-VCH, Weinheim, 2002, 463 pp.
- [2] V. Církva, M. Hájek, in: *Proceeding of the Conference of Microwave and High Frequency Heating*, Fermo, Italy, 1997, 153 pp.
- [3] V. Církva, M. Hájek, *J. Photochem. Photobiol. A: Chem.* 123 (1999) 21.
- [4] P. Klán, M. Hájek, V. Církva, *J. Photochem. Photobiol. A: Chem.* 140 (2001) 185.
- [5] P. Müller, P. Klán, V. Církva, *J. Photochem. Photobiol. A: Chem.* 158 (2003) 1.
- [6] S. Horikoshi, H. Hidaka, N. Serpone, *J. Photochem. Photobiol. A: Chem.* 159 (2003) 289.
- [7] M. Hájek, M.T. Radoiu, *J. Mol. Catal. A: Chem.* 160 (2000) 383.
- [8] M.T. Radoiu, M. Hájek, *J. Mol. Catal. A: Chem.* 186 (2002) 121.
- [9] R. Hermann, G.R. Mahalaxmi, T. Jochum, S. Naumov, O. Brede, *J. Phys. Chem. A* 106 (2002) 2379.
- [10] O. Brede, S. Naumov, R. Hermann, *Chem. Phys. Lett.* 355 (2002) 1.
- [11] E.J. Land, G. Porter, *Trans. Faraday Soc.* 59 (1963) 2016.
- [12] K. Okada, K. Okubo, M. Oda, H. Murai, *Chem. Lett.* 24 (1995) 845.
- [13] T. Matsuura, Y. Hiromoto, A. Okada, K. Ogura, *Tetrahedron* 29 (1973) 2981.
- [14] H.-I. Joschek, S.I. Miller, *J. Am. Chem. Soc.* 88 (1966) 3273.
- [15] P. Mazellier, M. Sarakha, A. Rossi, M. Bolte, *J. Photochem. Photobiol. A: Chem.* 115 (1998) 117.
- [16] M. Sarakha, M. Bolte, H.D. Burrows, *J. Photochem. Photobiol. A: Chem.* 107 (1997) 101.
- [17] D.R. Armstrong, C. Cameron, D.C. Nonhebel, P.G. Perkins, *J. Chem. Soc., Perkin Trans. 2* (1983) 587.
- [18] M. Tashiro, G. Fukata, *Org. Prep. Proced. Int.* 8 (1976) 241.
- [19] M. Tashiro, G. Fukata, *J. Org. Chem.* 42 (1977) 835.
- [20] M. Tashiro, G. Fukata, *J. Org. Chem.* 42 (1977) 428.
- [21] H. Hart, *J. Am. Chem. Soc.* 71 (1949) 1966.
- [22] A. Gilbert, J. Baggott (Eds.), *Essentials of Molecular Photochemistry*, Blackwell Science, Oxford, 1991.
- [23] G. Grabner, G. Köhler, J. Zechner, N. Getoff, *J. Phys. Chem.* 84 (1980) 3000.
- [24] G. Köhler, N. Getoff, *J. Chem. Soc., Faraday Trans. I* 72 (1976) 2101.
- [25] G. Grabner, G. Köhler, G. Marconi, S. Monti, E. Venuti, *J. Phys. Chem.* 94 (1990) 3609.
- [26] S. Dellonte, G. Marconi, *J. Photochem.* 30 (1985) 37.
- [27] N. Haga, H. Takayanagi, *J. Org. Chem.* 61 (1996) 735.
- [28] H.G.O. Becker (Ed.), *Einführung in die Photochemie*, DVW, Berlin, 1983, 486 pp.
- [29] S. Canonica, U. Jans, K. Stemmler, J. Hoigné, *Environ. Sci. Technol.* 29 (1995) 1822.
- [30] F. Magnaterra, P. Pedrielli, G.F. Pedulli, *Gazz. Chim. Ital.* 126 (1996) 673.