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Monoetherification of *tert*-Butylated Pyrocatechols upon Irradiation of Their Solutions in Hydrocarbons

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Abstract — Products of reactions of *tert*-butylated pyrocatechols with alkyl radicals were studied. The major products formed upon γ-irradiation of deaerated solutions of 4-*tert*-butyl- and 3,5-di-*tert*-butylpyrocatechol in hexane and cyclohexane are monoalkyl ethers, which were identified by NMR spectroscopy (^{1}H, ^{13}C, ^{1}H–^{1}H NOESY technique) and gas chromatography–mass spectrometry.

Alkylated pyrocatechols belong to the class of sterically hindered phenols and show promise as antioxidants both for important biological processes initiated by reactive substances and/or ionizing radiation and for stabilization of polymers, oils, etc. [1, 2]. The peroxy radicals are deactivated by hydrogen abstraction from the phenolic hydroxy group [1, 3]. Phenolic inhibitors also react with alkyl radicals and, under exposure to ionizing radiation, with H atoms and ionized solvent molecules [4, 5]:

$$H\ (R^{\cdot}) + PhOH \longrightarrow H_2\ (RH) + PhO^{\cdot},$$

$$RH^{\cdot+} + PhOH \rightarrow [RH + PhOH^{\cdot+}] \rightarrow PhO^{\cdot} + H^{+} + RH$$

This reaction is possible with both monohydric phenols and alkylated pyrocatechols, since their ionization potential (8–9 eV) is lower than that of hydrocarbons [6]. One of the pathways of consumption of phenoxy radicals is their recombination with alkyl radicals yielding various adducts. For example, it was shown previously that γ-irradiation of deaerated solutions of 2,6-di-*tert*-butyl-4-methylphenol (Ionol) in cyclohexane results in C-alkylation of Ionol [7]. At the same time, despite extensive use of antioxidants based on dihydric phenols, data on their reactions with carbon-centered radicals and on the structure of the reaction products are lacking.

The goal of this study was to identify the products formed from substituted pyrocatechols upon γ-irradiation of their deaerated solutions in hexane and cyclohexane as typical representatives of linear and cyclic hydrocarbons. Experiments were performed with 3,5-di-*tert*-butylpyrocatechol (**I**) and 4-*tert*-butylpyrocatechol (**II**).

It is known that γ-irradiation of hexane results in generation of radicals with the radical center at C^2 and C^3, and irradiation of cyclohexane, in generation of a single radical species [8]. Recombination of these radicals yields isomeric dodecanes and dicyclohexyl, respectively.

We have shown previously that 3,5-di-*tert*-butylpyrocatechol (**I**) efficiently suppresses formation of recombination products of hexyl radicals [9, 10]. To elucidate the structure of transformation products of pyrocatechols, we examined the influence of their concentration on the radiation-chemical yields of adducts in hexane and cyclohexane. This allowed optimization of the irradiation conditions. As seen from the table, at the maximum possible concentration of **I** in hydrocarbons, equal to 1×10^{-2} M, the yield of dodecanes decreases to 0.11, and that of dicyclohexyl, to 0.20 molecule/100 eV, with the yield of decomposition of **I** being 4.5 molecules/100 eV in hexane and 3.8 molecules/100 eV in cyclohexane. According to GLC, the pyrocatechol is completely consumed after irradiation for 16–20 h, with the yield of addition products being 2.6 and 2.2 molecules/100 eV for hexyl and cyclohexyl radicals, respectively.

The optimal concentration of **II** was 5×10^{-3} M, since at a higher concentration (10^{-2} M) the pyrocatechol was consumed in a considerably longer time, which resulted in increased yield of secondary products.

According to GC–MS analysis, irradiation of **I** in hexane yielded two major products giving a molecular peak at *m/z* 306. The ^{1}H NMR spectrum of the products isolated by column chromatography contains OCH proton signals (a sextet at 4.21 and a quintet at 4.37 ppm), and the ^{13}C NMR spectrum contains the OCH carbon signals at 75.44 and 80.17 ppm, which

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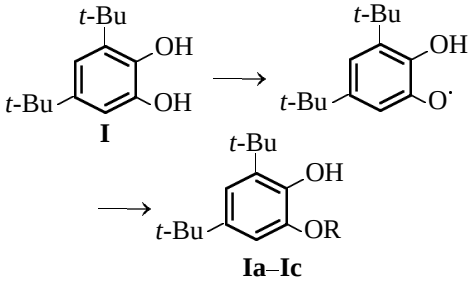
Radiation-chemical yields of addition products and yields of decomposition of 3,5-di-*tert*-butylpyrocatechol **I** and 4-*tert*-butylpyrocatechol **II** as influenced by the solvent and pyrocatechol concentration

Pyrocatechol	Solvent	Pyrocatechol concentration, M	Yield, molecule/100 eV			Time of pyrocatechol consumption, h
			recombination products	pyrocatechol decomposition products	addition products	
	Hexane	–	0.76	–	–	–
	Cyclohexane	–	0.86	–	–	–
I	Hexane	5×10^{-3}	0.14	3.0	2.2	10
		1×10^{-2}	0.11	4.5	2.6	16
	Cyclohexane	5×10^{-3}	0.28	2.8	1.8	12
		1×10^{-2}	0.20	3.8	2.2	20
II	Hexane	2×10^{-3}	0.20	1.3	1.2	8
		5×10^{-3}	0.15	2.6	1.6	18
		1×10^{-2}	0.13	3.0	2.2	30
	Cyclohexane	2×10^{-3}	0.40	3.0	1.4	8
		5×10^{-3}	0.40	2.7	1.6	20
		1×10^{-2}	0.30	1.8	1.6	40

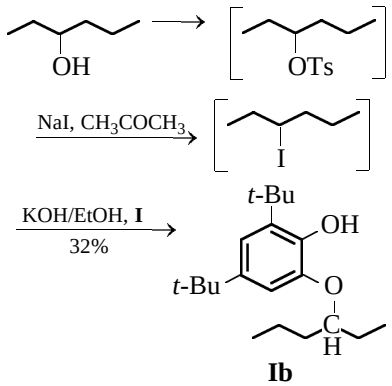
corresponds to the structure of 2- and 3-hexyl ethers **Ia** and **Ib**.



Ia–**Ic**

R = 2-hexyl (**a**), 3-hexyl (**b**), and cyclohexyl (**c**).

The structure of **Ib** was confirmed by independent synthesis:



Ib

The tosylate and iodide were prepared according to [11], and ether **Ib**, according to [12]. Comparison of the ^{1}H and ^{13}C NMR spectra of **Ib** with the spectra of the products isolated after irradiation allows assignment of the signals of **Ia**.

Irradiation of **I** in cyclohexane, according to GC–MS analysis, yielded a complex mixture of adducts that mainly consisted of products giving molecular peaks at *m/z* 304 and 386. The mixture was fractionated by column chromatography. One of the fractions (30 mg) contained two products in a 4 : 1 ratio (molecular peak at *m/z* 304, intensity 6.43 and 1.51%, respectively). The fragment peak at *m/z* 222, characteristic of both products, suggests formation of monoalkyl ethers [13]. Since in cyclohexane only a single radical species is generated, we presumed that these products differed in the alkylation site (nonequivalent OH groups). The ^{1}H NMR spectrum contained two OH singlets (δ 6.04 and 6.06 ppm) and a multiplet of the OCH proton (δ 4.2–4.3 ppm). The structure of one of the products was confirmed by independent synthesis from **I** and cyclohexyl bromide according to [12]. In addition, we isolated a fraction with R_f 0.25 (20 mg), which, according to GC–MS analysis, consisted of three compounds giving a molecular peak at *m/z* 386. This corresponds to addition of two cyclohexyl radicals to **I**. These compounds are secondary products; we failed to prove their structure.

Irradiation of **II** in hexane yielded a mixture of

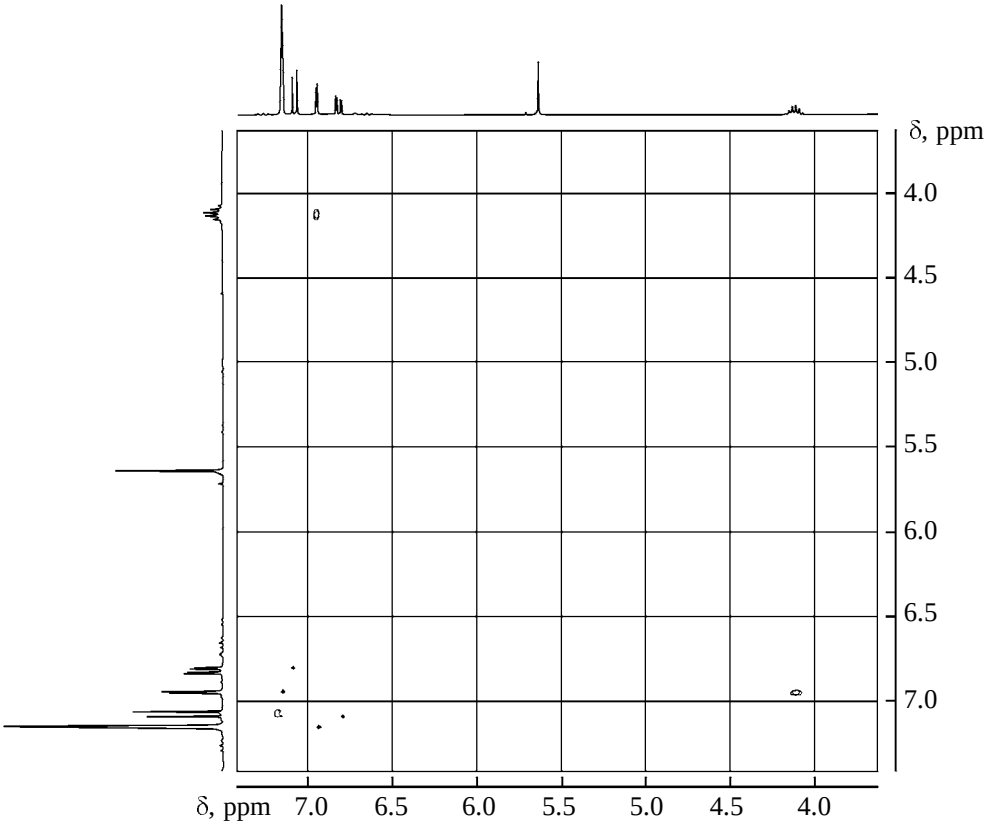
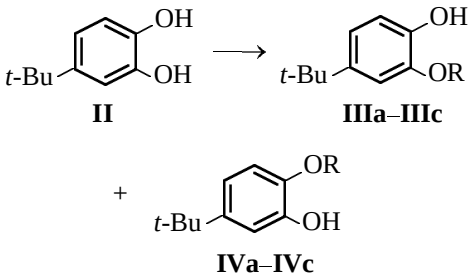


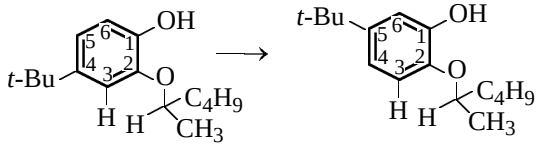
Fig. 1. Fragment of the two-dimensional ^1H–^1H NOESY NMR spectrum of 2-(2-hexyloxy)-4-*tert*-butylphenol.

products. After chromatographic separation, two fractions were obtained, one of which, according to GC–MS analysis, contained four compounds giving the molecular peak at *m/z* 250 and the fragmentation pattern typical of ethers.



R = 2-hexyl (**a**), 3-hexyl (**b**), cyclohexyl (**c**).

The ^1H NMR spectrum contained the OH signals at δ 5.58, 5.60, 5.66, and 5.69 ppm and OCH multiplets at δ 4.18–4.29 and 4.32–4.45 ppm. The ^{13}C NMR spectrum contained the ether carbon signals at δ_C 75.41 and 80.15 ppm, confirming the presence of ethers in this fraction. The structure of compounds **IIIa**, **IIIb**, **IVa**, and **IVb** was confirmed by their comparison with the respective authentic samples prepared by the reaction of 4-*tert*-butylpyrocatechol with 2- and 3-hexyl iodide. The mixture of two isomers was chromatographed on a silica gel column (eluent hexane–CH_2Cl_2, 2 : 1). The signals in the ^1H NMR spectra of 4- and 5-*tert*-butyl-2-(2-hexyloxy)phenols were assigned using two-dimensional ^1H–^1H NOESY NMR spectroscopy. The observation of cross peaks between the OCH multiplet (δ 4.10 ppm) and the doublet of the H^3 proton of the ring (δ 6.95 ppm, *J* 2.15 Hz) corresponds to the structure of 2-(2-hexyloxy)-4-*tert*-butylphenol **IIIa** (Fig. 1). In the case of 2-(2-hexyloxy)-5-*tert*-butylphenol **IVa**, a cross peak is also observed between the OCH multiplet (δ 4.25 ppm) and an H^3 doublet (δ 6.66 ppm), but in this case the coupling is vicinal, and *J* is as high as 8.55 Hz (Fig. 2).



γ-Irradiation of 4-*tert*-butylpyrocatechol **II** in cyclohexane also yielded, according to GC–MS analysis, a complex mixture of adducts of **II** with cyclohexane. The mixture was fractionated by column chromatography; one of the fractions contained two products,

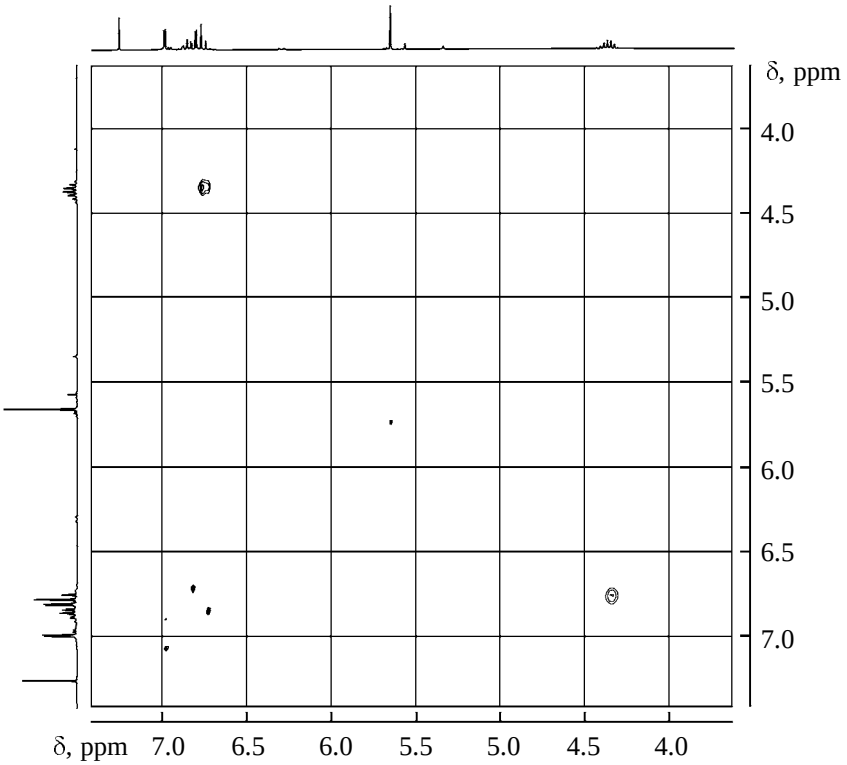


Fig. 2. Fragment of the two-dimensional ^1H–^1H NOESY NMR spectrum of 2-(2-hexyloxy)-5-*tert*-butylphenol.

both giving a molecular peak at *m/z* 250 and a fragment peak at *m/z* 166. The ^1H NMR spectrum of this fraction showed the presence of two compounds. The spectrum contained the signals of aromatic and OH (δ 5.58 and 5.65 ppm) protons and a multiplet of the OCH group in two compounds at δ 4.20–4.27 ppm. In the ^{13}C NMR spectrum, the OCH carbon signals from both compounds coincided and were observed at 76.5 ppm. The coincidence of the signals in the ^1H and ^{13}C NMR spectra of the compounds obtained by independent synthesis (reaction of **II** with cyclohexyl bromide [12]) with those of the compounds isolated chromatographically allows identification of the products as **IIIc** and **IVc**.

In the isolated fractions, the compounds giving a molecular peak at *m/z* 330 were present in significant amounts. This molecular weight corresponds to addition of two hexyl or cyclohexyl radicals. Thus, these are the secondary transformation products of the ethers.

Thus, the major products formed upon γ-irradiation of pyrocatechols **I** and **II** in hydrocarbons are the corresponding monoalkyl ethers.

EXPERIMENTAL

Compound **I** was prepared as described in [8]. Compound **II** was recrystallized from petroleum ether. Solvents were purified to remove unsaturated impurities according to [14].

The reaction progress was monitored by TLC on Macherey Nagel, Alugram sil G/UV-254 plates with fluorescent indicator. The plates were developed in I_2 vapor or in alcoholic solution of phosphomolybdic acid, with subsequent heating to 120°C. The products were separated on a column packed with silica gel (Merck, Kieselgel 60 and Baker analyzed, 20–45 μm). The IR spectra were recorded on a Perkin–Elmer Spektrum IR-1000FT spectrophotometer (thin film). The ^1H and ^{13}C NMR spectra were taken on a Bruker AM-250 spectrometer (working frequencies 250 and 62.9 MHz, respectively) in $CDCl_3$ and C_6D_6. The proton chemical shifts were determined relative to chloroform (δ 7.26, δ_C 77.0 ppm) and C_6D_6 (δ 7.15, δ_C 128.0 ppm). Isomers **IIIa**, **IIIb**, **IVa**, and **IVb** were identified independently on the basis of direct observation of the Overhauser effect for sterically proximate protons. The two-dimensional ^1H–^1H NOESY NMR spectra were measured in $CDCl_3$ and C_6D_6 (Bruker AMŒ-300). The ^{13}C NMR signals were assigned using the DEPT technique: CH and CH_3 (+), CH_2 (–), C (0). Identification of products by retention times was performed with a Shimadzu GC-17A gas–liquid chromatograph (SE-54 25 000 × 0.25-mm quartz capillary column) directly connected to a QP-5000 mass spectrometer. The column was heated

from 100 to 280°C at a rate of 5 deg min^{-1}. The carrier gas was helium (0.8 ml min^{-1}).

Sample preparation and irradiation. Alkylated pyrocatechol **I** or **II** was dissolved in hexane (or cyclohexane); the solution was deaerated and irradiated in sealed glass ampules with ^{137}Cs radiation from an LMB-γ-1M installation at a dose rate of 0.35 Gy s^{-1} to a dose of 25 kGy (20 h). The solvent was removed on a rotary evaporator, and the remaining yellow oil was chromatographed on a column (silica gel, hexane–AcOEt, 40 : 1).

Isolation of hexyl ethers Ia and Ib after γ-irradiation. From 40 mg of **I** and 20 ml of hexane, we obtained 32 mg (43%) of a mixture of two products in a 52 : 48 ratio (GLC). Since we failed to separate these compounds by column chromatography, they were characterized by independent synthesis.

2-(3-Hexyloxy)-4,6-di-*tert*-butylphenol (Ib). Tosyl chloride (2.06 g) was added to a solution of 1.00 g of 3-hexanol in 8 ml of pyridine, cooled to 0°C. The mixture was stirred for 2 h at 0°C and then for 3 h at room temperature. After that, 150 ml of cold water was added, and the liquid was extracted with ether (4 × 50 ml). The combined ether extracts were washed with 10% HCl (2 × 50 ml) and saturated $NaHCO_3$ solution (3 × 50 ml) and dried over $MgSO_4$. The solvent was distilled off, the remaining oil (3.95 g) was dissolved in 61 ml of acetone, and 6.1 g of NaI was added. The reaction mixture was stirred for 18 h at room temperature, after which the precipitate was filtered off, the filtrate was poured into 100 ml of H_2O, and the mixture was extracted with ether (4 × 50 ml). The combined extracts were washed with 50 ml of 10% Na_2SO_3 and dried over $MgSO_4$. The solvent was distilled off, and the remaining oil (1.17 g) was added to a mixture obtained in a nitrogen atmosphere from a solution of 0.27 g of KOH in 2.8 ml of 96% ethanol and 0.247 g of 3,5-di-*tert*-butylpyrocatechol. The mixture was refluxed for 3 h, diluted with water, acidified with HCl, extracted with ethyl acetate (3 × 20 ml), and dried over $MgSO_4$. After removing the solvent in a vacuum, the remaining dark oil was chromatographed on SiO_2 (eluent hexane–AcOEt, 40 : 1). The main fraction (0.128 g) was distilled in a vacuum (150°C, 0.01 mm Hg, Kugelrohr), and 0.108 g of ether **Ib** was isolated (yield 32% based on **I**).

2-(3-Hexyloxy)-4,6-di-*tert*-butylphenol Ib. R_f 0.63 (hexane–AcOEt, 10 : 1). IR spectrum, ν, cm^{-1}: 3650, 1260. ^1H NMR spectrum, δ, ppm (*J*, Hz): 0.97 t (3H, CH_3, *J* 7.1), 0.99 t (3H, CH_3, *J* 7.1), 1.32 s (9H, *t*-Bu), 1.43 s (9H, *t*-Bu), 1.25–1.78 m (6H, CH_2), 4.23 quintet (1H, OCH, *J* 7.3), 6.04 s (1H, OH), 6.79 d (1H, ArH, *J* 2.08), 6.92 d (1H, ArH, *J* 2.08). ^{13}C NMR spectrum, δ_C, ppm: 9.57 (+) (CH_3), 14.19 (+) (CH_3), 18.65 (–) (CH_2), 26.67 (–) (CH_2), 29.48 (+) (*t*-Bu), 31.66 (+) (*t*-Bu), 34.51 (0), 34.84 (0), 35.70 (–) (CH_2), 80.23 (+) (OCH), 108.22 (+) (C^5), 115.43 (+) (C^3), 134.41 (0) (C^6), 140.98 (0) (C^4), 142.73 (0) (C^2), 144.55 (0) (C^1). Mass spectrum, *m/z* (I_{rel}, %): 306 (7.8) $[M]^+$, 222 (38.0) $[M - C_6H_{12}]^+$, 207 (100) $[M - C_6H_{12} - CH_3]^+$.

2-(2-Hexyloxy-4,6-di-*tert*-butylphenol Ia. R_f 0.60 (hexane–AcOEt, 10 : 1). IR spectrum, ν, cm^{-1}: 3650, 1260. ^1H NMR spectrum, δ, ppm (*J*, Hz): 0.94 t (3H, CH_3, *J* 6.8), 0.96 t (3H, CH_3, *J* 7.4), 1.29 s (9H, *t*-Bu), 1.40 s (9H, *t*-Bu), 1.25–1.78 m (6H, CH_2), 4.37 sextet (1H, OCH, *J* 6.0), 5.99 s (1H, OH), 6.77 d (1H, ArH, *J* 2.08), 6.89 d (1H, ArH, *J* 2.08). ^{13}C NMR spectrum, δ_C, ppm: 14.05 (+) (CH_3), 20.03 (+) (CH_3), 22.68 (–) (CH_2), 27.73 (–) (CH_2), 29.45 (+) (*t*-Bu), 31.65 (+) (*t*-Bu), 34.51 (0), 34.83 (0), 36.29 (–) (CH_2), 75.44 (+) (OCH), 108.26 (+) (C^5), 115.50 (+) (C^3), 134.42 (0) (C^6), 141.09 (0) (C^4), 142.74 (0) (C^2), 144.18 (0) (C^1). Mass spectrum, *m/z* (I_{rel}, %): 306 (6.8) $[M]^+$, 222 (37.6) $[M - C_6H_{12}]^+$, 207 (100) $[M - C_6H_{12} - CH_3]^+$.

Isolation of 2-cyclohexyloxy-4,6-di-*tert*-butylphenol Ic after γ-irradiation. After γ-irradiation of a deaerated solution of 40 mg of **I** in 20 ml of cyclohexane, removal of the solvent on a rotary evaporator, and chromatography of the residue (60 mg; silica gel, hexane–AcOEt, 40 : 1), we obtained 24 mg (43%) of ether **Ic** (R_f 0.56) and 6.0 mg (10%) of an isomer with R_f 0.47 (hexane–AcOEt, 10 : 1).

2-Cyclohexyloxy-4,6-di-*tert*-butylphenol (Ic). In a nitrogen atmosphere, 0.50 g of **I** was dissolved in a solution of 0.27 g of KOH in 2.8 ml of 96% EtOH. Cyclohexyl bromide (1.06 g) was added; the mixture was refluxed with stirring for 4 h and worked up as described above for **Ib**. After chromatography (silica gel, hexane–AcOEt, 40 : 1), 0.12 g (18%) of **Ic** was obtained. R_f 0.56 (hexane–AcOEt, 10 : 1). IR spectrum, ν, cm^{-1}: 3513, 1299. ^1H NMR spectrum, δ, ppm (*J*, Hz): 1.29 s (9H, *t*-Bu), 1.40 s (9H, *t*-Bu), 1.20–2.17 m (10H, CH_2), 4.19–4.29 m (1H, OCH), 6.04 s (1H, OH), 6.80 d (1H, ArH, *J* 2.1), 6.90 d (1H, ArH, *J* 2.1). ^{13}C NMR spectrum, δ_C, ppm: 23.70 (–) (CH_2), 25.51 (–) (CH_2), 29.45 (+) (*t*-Bu), 31.66 (+) (*t*-Bu), 32.08 (–) (CH_2), 34.48 (0), 34.83 (0), 77.10 (+) (OCH), 108.69 (+) (C^5), 115.67 (+) (C^3), 134.50 (0) (C^6), 141.09 (0) (C^4), 142.89 (0) (C^2), 143.94 (0) (C^1). Mass spectrum, *m/z* (I_{rel}, %): 304 (6.4) $[M^+]$, 222 (32.1) $[M - C_6H_{10}]^+$, 207 (100) $[M - C_6H_{10} - CH_3]^+$.

Isolation of hexyl ethers IIIa, IIIb, IVa, and IVb after γ-irradiation. After γ-irradiation of a deaerated

solution of 40 mg of **II** in 50 ml of hexane, removal of the solvent on a rotary evaporator, and chromatography of the residue (52 mg) on silica gel (eluent hexane–AcOEt, 40 : 1), 27 mg of a fraction with R_f 0.56 was obtained. According to GC–MS analysis, the fraction consisted of four products giving a molecular peak at *m/z* 250; it was a mixture of four monoalkyl ethers. The total chemical yield of **IIIa**, **IIIb**, **IVa**, and **IVb** was 43%. Since we failed to separate these compounds by column chromatography, they were characterized by independent synthesis.

2-(2-Hexyloxy-5-*tert*-butylphenol IVa and 2-(2-hexyloxy)-4-*tert*-butylphenol (IIIa). From compound **II** and 2-hexyl iodide [15], we obtained a mixture of **IIIa** and **IVa** according to [12] in a total yield of 45 mg (45%). The ethers were separated by column chromatography (Baker silica gel, eluent hexane–CH_2Cl_2, 2 : 1) and characterized by ^1H, ^{13}C, and ^1H–^1H NOESY NMR spectroscopy.

2-(2-Hexyloxy)-5-*tert*-butylphenol (IVa). ^1H NMR spectrum, δ, ppm (*J*, Hz): 0.92 t (3H, CH_3, *J* 6.8), 1.29 s (9H, *t*-Bu), 1.30 d (3H, CH_3, *J* 6.3), 1.25–1.78 m (4H, CH_2), 1.80–2.12 m (2H, CH_2), 4.37 sextet (1H, OCH, *J* 5.7), 5.67 s (1H, OH), 6.76 d (1H, Ar–H^3, $J_{3,4}$ 8.6), 6.82 d.d (1H, Ar–H^4, $J_{3,4}$ 8.6 and $J_{4,6}$ 2.1), 7.00 d (1H, Ar–H^6, $J_{4,6}$ 2.2). ^{13}C NMR spectrum, δ_C, ppm: 9.54 (+) (CH_3), 18.65 (–) (CH_2), 26.60 (–) (CH_2), 31.44 (+) (*t*-Bu), 34.19 (0), 35.66 (–) (CH_2), 80.17 (+) (OCH), 112.03 (+) (C^3), 112.34 (+) (C^6), 116.35 (+) (C^5), 142.94 (0) (C^2), 144.55 (0) (C^1), 145.81 (0) (C^4). Mass spectrum, *m/z* (I_{rel}, %): 250 (5.9) $[M]^+$, 166 (21.0) $[M - C_6H_{12}]^+$, 151 (100) $[M - C_6H_{12} - CH_3]^+$.

2-(2-Hexyloxy)-4-*tert*-butylphenol (IIIa). ^1H NMR spectrum (C_6D_6), δ, ppm (*J*, Hz): 0.8 t (3H, CH_3, *J* 6.6), 1.0 d (3H, CH_3, *J* 6.0), 1.00–1.60 m (6H, CH_2), 1.25 s (9H, *t*-Bu), 4.10 sextet (1H, OCH, *J* 6.0), 5.50 s (1H, OH), 6.81 d.d (1H, Ar–H^5, $J_{5,3}$ 2.2, $J_{5,6}$ 8.3), 6.94 d (1H, Ar–H^3, $J_{3,5}$ 2.2), 7.07 d (1H, Ar–H^6, $J_{6,5}$ 8.3). ^{13}C NMR spectrum, δ_C, ppm: 9.54 (+) (CH_3), 18.65 (–) (CH_2), 26.60 (–) (CH_2), 31.44 (+) (*t*-Bu), 34.19 (0), 33.56 (–) (CH_2), 80.17 (+) (OCH), 112.03 (+) (C^3), 112.34 (+) (C^6), 116.35 (+) (C^5), 142.94 (0) (C^2), 144.55 (0) (C^1), 145.81 (0) (C^4). Mass spectrum, *m/z* (I_{rel}, %): 250 (6.2) $[M]^+$, 166 (19.4) $[M - C_6H_{12}]^+$, 151 (100) $[M - C_6H_{12} - CH_3]^+$.

2-(3-Hexyloxy)-5-*tert*-butylphenol (IVb). ^1H NMR spectrum, δ, ppm (*J*, Hz): 0.92 t (3H, CH_3, *J* 7.2), 0.95 t (3H, CH_3, *J* 7.4), 1.34–1.53 m (2H, CH_2), 1.57–1.74 m (4H, CH_2), 4.19 quintet (1H, OCH, *J* 5.8), 5.67 s (1H, OH), 6.74 d (1H, Ar–H^3, $J_{3,4}$ 8.6), 6.82 d.d (1H, Ar–H^4, $J_{3,4}$ 8.6 and $J_{4,6}$ 2.1), 6.98 d (1H, Ar–H^6, $J_{4,6}$ 2.2). ^{13}C NMR spectrum, δ_C, ppm: 9.54 (+) (CH_3), 18.65 (–) (CH_2), 26.60 (–) (CH_2), 31.44 (+) (*t*-Bu), 34.19 (0), 35.66 (–) (CH_2), 80.17 (+) (OCH), 112.03 (+) (C^3), 112.34 (+) (C^6), 116.35 (+) (C^5), 142.94 (0) (C^2), 144.55 (0) (C^1), 145.81 (0) (C^4). Mass spectrum, *m/z* (I_{rel}, %): 250 (5.2) $[M]^+$, 166 (20.8) $[M - C_6H_{12}]^+$, 151 (100) $[M - C_6H_{12} - CH_3]^+$.

Isolation of 4-*tert*-butylpyrocatechol cyclohexyl ethers IIIc and IVc after γ-irradiation. After γ-irradiation of a deaerated solution of 40 mg of **II** in 50 ml of cyclohexane, solvent evaporation on a rotary evaporator, and chromatography of the residue (67 mg) on silica gel (eluent hexane–AcOEt, 40 : 1), a fraction (22 mg) with R_f 0.56 was isolated. According to GC–MS analysis, the fraction consisted of two compounds giving a molecular peak at *m/z* 248 and was a mixture of monoalkyl ethers **IIIc** and **IVc** (total yield 35%).

A mixture of **IIIc** and **IVc** was independently obtained from **II** and cyclohexyl bromide according to [12] in 17% yield after column chromatography (SiO_2, hexane–AcOEt, 40 : 1). The signals in the spectra of **IIIc** and **IVc** were assigned by comparison with the spectra of pure **IIIa** and **IVa**.

2-Cyclohexyloxy-5-*tert*-butylphenol (IVc). R_f 0.56 (hexane–AcOEt, 10 : 1). IR spectrum, ν, cm^{-1}: 3513, 1299. ^1H NMR spectrum, δ, ppm (*J*, Hz): 1.27 s (9H, *t*-Bu), 1.20–2.10 m (10H, CH_2), 4.20–4.27 m (1H, OCH), 5.65 s (1H, OH), 6.80 s (2H, ArH), 7.00 s (1H, ArH). ^{13}C NMR spectrum, δ_C, ppm: 23.80 (–) (CH_2), 26.37 (–) (CH_2), 31.44 (+) (*t*-Bu), 32.02 (–) (CH_2), 34.20 (0), 76.50 (+) (OCH), 112.09 (+), 112.99 (+), 116.38 (+), 142.14 (0), 144.41 (0), 146.02 (0).

2-Cyclohexyloxy-4-*tert*-butylphenol IIIc. R_f 0.56 (hexane–AcOEt, 10 : 1). IR spectrum, ν, cm^{-1}: 3513, 1299. ^1H NMR spectrum, δ, ppm (*J*, Hz): 1.29 s (9H, *t*-Bu), 1.20–2.10 m (10H, CH_2), 4.20–4.27 m (1H, OCH), 5.58 s (1H, OH), 6.87 s (2H, ArH), 6.91 s (1H, ArH). ^{13}C NMR spectrum, δ_C, ppm: 23.73 (–) (CH_2), 25.49 (–) (CH_2), 31.57 (+) (*t*-Bu), 32.06 (–) (CH_2), 34.29 (0), 77.5 (+) (OCH), 111.44 (+), 113.77 (+), 118.04 (+), 143.12 (0), 143.82 (0), 144.72 (0). Mass spectrum, *m/z* (I_{rel}, %): 248 (6.5) $[M]^+$, 166 (24.0) $[M - C_6H_{10}]^+$, 151 (100) $[M - C_6H_{10} - CH_3]^+$.

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