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Synthesis of New Primary-Tertiary Alkyl Bisperoxides by Reaction of Tertiary Hydroperoxides with Bromoalkanes in a PTC System

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Summary. Syntheses of novel primary-tertiary bisperoxides were carried out under phase transfer catalysis conditions. The bisperoxides were obtained in good yields, the reaction times not exceeding four hours.

Keywords. Peroxides; Initiators; PTC.

Introduction

In recent years the production of chemicals displayed a noticeable increase, particularly the production of fine chemicals. A considerable part of this kind of production comprises auxiliary substances applied in the synthesis and processing of plastics. Representatives of this group are organic peroxides which are used as polymerization initiators and crosslinking agents [1]. Recently, growing interest in compounds containing several peroxide and/or azo groups has been observed [2]. These compounds may be used as precursors in the free-radical synthesis of block and graft copolymers.

One method to prepare alkyl peroxides is based on phase transfer catalysis [3, 4]. These reactions are characterized by high efficiency and selectivity, accompanied by a shortening of the reaction time compared to analogous reactions carried out in homogeneous systems. It was the purpose of this investigation to synthesize new primary-tertiary alkyl bisperoxides (Scheme 1) under phase transfer catalysis conditions.

Results and Discussion

Bisperoxides **5**–**8** were obtained by reaction of the sodium salts of cumene hydroperoxide (**1**) or 2-(1-hydroperoxy-1-methylethyl)-naphthalene (**2**) with 1,4-dibromobutane (**3**) or 1,10-dibromodecane (**4**). The bisperoxides **12** and **13** resulted from

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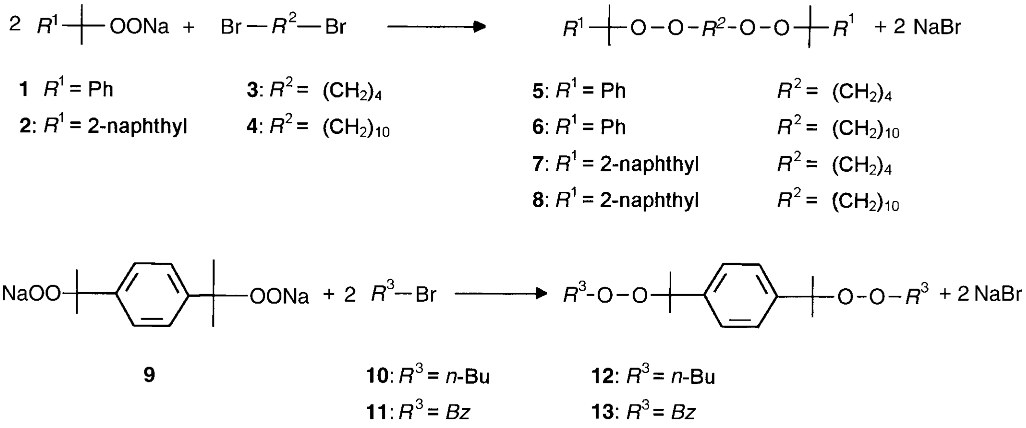

Scheme 1

the reaction of the disodium salt of 1,4-*bis*-(1-hydroperoxy-1-methylethyl)-benzene (**9**) with bromobutane (**10**) or benzyl bromide (**11**).

The synthesis of peroxides **5** and **6** in a homogenous system (anhydrous EtOH) has been claimed in patents [5, 6]; the other peroxides are novel compounds. The bisperoxides were obtained in satisfactory yields, especially when compared to those obtained in homogenous systems. The reaction time of 4 hours was almost four times shorter than that for similar reactions performed in homogenous systems [5].

Experimental

Bromobutane (**10**; 98%, P.P.H. POCh Gliwice), 1,4-dibromobutane (**3**; 98%, Merck), 1,10-dibromodecane (**4**; 99%, Merck), benzyl bromide (**13**; 98%, Merck), tetra-*n*-butylammonium hydrogensulfate (98%, Merck), and 1,4-*bis*-(1-hydroxy-1-methylethyl)-benzene (99%, Aldrich) were used without further purification. The results of elemental analyses agreed favourably with the calculated values. NMR spectra were recorded on a Varian Inova 300 multinuclear NMR spectrometer in $CDCl_3$ using *TMS* as internal standard.

1,4-Bis-(1-hydroperoxy-1-methylethyl)-benzene

1,4-*Bis*-(1-hydroperoxy-1-methylethyl)-benzene was prepared from 1,4-*bis*-(1-hydroxy-1-methylethyl)-benzene by reaction with 63% H_2O_2 and H_2SO_4 as a catalyst. In a thermostatted 500 cm^3 round-bottomed flask equipped with a thermometer, a mechanical stirrer, and a reflux condenser, 20 g 1,4-*bis*-(1-hydroxy-1-methylethyl)-benzene (103 mmol) and 200 cm^3 toluene were heated to 50°C; then, a solution of 41 cm^3 63% H_2O_2 (610 mmol) and 0.04 cm^3 98% H_2SO_4 (8 mmol) was added in small portions. The reaction was complete after 5 h. The precipitate was filtered off, washed with H_2O, a saturated solution of $(NH_4)_2SO_4$, and again with H_2O. The crude product was then purified by recrystallization from benzene to give 20.73 g of a white solid (99%; m.p.: 146.5–147.5°C; Ref. [7]: m.p.: 147–152°C).

Disodium salt of 1,4-bis-(1-hydroperoxy-1-methylethyl)-benzene (**9**; $C_{12}H_{16}O_4Na_2$)

A thermostatted 250 cm^3 round-bottomed flask equipped with a mechanical stirrer, a thermometer, and a $CaCl_2$ tube was charged with 5.56 g of 1,4-*bis*-(1-hydroperoxy-1-methylethyl)-benzene (25 mmol) and 76 cm^3 of anhydrous MeOH. The temperature of the mixture was lowered to −6°C, and 36 cm^3 of a 15 M methanolic solution of NaOH (55 mmol) was added dropwise over 2 h. The reaction mixture was then stirred at -6°C for 30 min. After completion of the reaction, the crude product was precipitated from acetone to give 3.12 g of a white hygroscopic crystalline solid (yield: 37%, purity: 98% based on iodometric analysis and acidimetric titration).

Sodium salt of cumene hydroperoxide (**1**), *Sodium salt of 2-(1-hydroperoxy-1-methylethyl)-naphthalene* (**2**)

1 and **2** were obtained by reaction of an aqueous solution of NaOH (50%) with solutions of cumene hydroperoxide (65% in toluene) and 2-(1-hydroperoxy-methylethyl)-naphthalene (46% in toluene) in analogy to the methods described in Refs. [8] and [9].

Preparation of peroxides **5–8**; *general procedure*

In an 80 cm^3 thermostatted reactor fitted with a magnetic stirrer, a reflux condenser, and a thermometer, 10 mmol of the sodium salt of the hydroperoxide and 2 mmol of catalyst (tetrabutylammonium hydrogensulfate) were dissolved in 10 cm^3 of benzene or toluene. The bromoalkane (5 mmol) was added dropwise at 20°C under stirring, and the reaction mixture was then heated to 50°C with stirring. The progress of reaction was monitored by iodometric analysis (concentration of hydroperoxide) [10], thin layer chromatography, and ^{1}H NMR spectroscopy. After completion of the reaction, the mixture was poured into 20 cm^3 H_2O, and the organic phase was separated, washed with H_2O until Br^- was absent (test with 0.01 M $AgNO_3$), and finally dried over anhydrous $MgSO_4$. After removal of the solvent under vacuum, the crude material was purified by column chromatography (silica gel, Merck, 70–230 mesh) using $CHCl_3$ as eluent.

1,4-Bis-(1-methyl-1-phenylethyl-dioxy)-butane (**5**; $C_{22}H_{30}O_4$)

Yield: 85%; n_D^{20}: 1.5206; ^{1}H NMR ($CDCl_3$, δ, 300 MHz): 7.46–7.24 (m, 10H, H_{ar}), 3.86 (t, $J =$ 5.5 Hz, 4H, –O–O–CH_2–CH_2–), 1.57 (s, 12H, Ar–C(CH_3)$_2$–O–O–), 1.53 (t, $J = 5.5$ Hz, 4H, –O–O–CH_2–CH_2–) ppm; ^{13}C NMR ($CDCl_3$, δ, 75 MHz): 145.4, 128.0, 127.0, 125.4 (C_{ar}), 82.6 (Ar–C(CH_3)$_2$–O–O–), 74.3 (–O–O–CH$_2$–CH_2–), 26.5 (–C(CH$_3$)$_2$–O–O–), 24.6 (–O–O–CH_2–CH$_2$–) ppm.

1,10-Bis-(1-methyl-1-phenylethyl-dioxy)-decane (**6**; $C_{28}H_{42}O_4$)

Yield: 80%; n_D^{20}: 1.5087; ^{1}H NMR ($CDCl_3$, δ, 300 MHz): 7.48–7.22 (m, 10H, H_{ar}), 3.90 (t, $J = 6.6$ Hz, 4H, –O–O–CH_2–CH_2–), 1.58 (s, 12H, Ar–C(CH_3)$_2$–O–O–), 1.52 (m, 4H, –O–O–CH_2–CH_2–), 1.20 (s, 12H, –O–O–(CH_2)$_2$–(CH_2)$_3$–) ppm; ^{13}C NMR ($CDCl_3$, δ, 75 MHz): 145.5, 128.0, 127.0, 125.5 (C_{ar}), 82.6 (–C(CH_3)$_2$–O–O–), 74.9 (–O–O–CH$_2$–CH_2–), 29.5, 29.4, 27.9, 26.2 (–O–O–CH_2–(CH$_2$)$_4$), 26.6 (–C(CH$_3$)$_2$–O–O–) ppm.

1,4-Bis-(1-methyl-1-(2-naphthyl)-ethyldioxy)-butane (**7**; $C_{30}H_{34}O_4$)

Yield: 87%; m.p.: 44–47°C; ^{1}H NMR ($CDCl_3$, δ, 300 MHz): 7.83–7.41 (m, 14H, H_{ar}), 3.86 (t, $J = 5.7$ Hz, 4H, –O–O–CH_2–CH_2–), 1.64 (s, 12H, Ar–C(CH_3)$_2$–O–O–), 1.52 (t, $J = 5.7$ Hz, 4H, –O–O–CH_2–CH_2–) ppm; ^{13}C NMR ($CDCl_3$, δ, 75 MHz): 143.0, 133.1, 132.4, 128.2, 127.6, 127.4, 125.9, 125.7, 124.2, 124.0 (C_{ar}), 82.7 (–C(CH_3)$_2$–O–O–), 74.4 (–O–O–CH$_2$–CH_2–), 26.5 (–C(CH$_3$)$_2$–O–O–), 24.6 (–O–O–CH_2–CH$_2$–) ppm.

1,10-Bis-(1-methyl-1-(2-naphthyl)-ethyldioxy)-decane (**8**; $C_{36}H_{46}O_4$)

Yield: 85%; n_D^{20}: 1.5504; ^{1}H NMR ($CDCl_3$, δ, 300 MHz): 7.78–7.35 (m, 14H, H_{ar}), 3.84 (t, $J = 6.6$ Hz, 4H, –O–O–CH_2–CH_2–), 1.61 (s, 12H, Ar–C(CH_3)$_2$–O–O–), 1.45–1.02 (m, 16H,

–O–O–CH$_2$–(C*H*$_2$)$_4$–) ppm; ^{13}C NMR (CDCl$_3$, δ, 75 MHz): 143.0, 133.1, 132.5, 128.2, 127.6, 127.4, 125.9, 125.7, 124.2, 124.0 (C$_{ar}$), 82.7 (–*C*(CH$_3$)$_2$–O–O–), 74.5 (–O–O–*C*H$_2$–CH$_2$–), 29.7, 29.3, 27.9, 26.2 (–O–O–CH$_2$–(*C*H$_2$)$_4$–), 26.6 (–C(*C*H$_3$)$_2$–O–O–) ppm.

Preparation of peroxides **12** *and* **13**; *general procedure*

In an 80 cm^3 reactor equipped with a magnetic stirrer, a reflux condenser, and a thermometer, 5 mmol of the sodium salt of the dihydroperoxide and 1 mmol of catalyst were dissolved in 10 cm^3 of benzene or toluene. Then, 10 mmol of the bromoalkane were added dropwise at 20°C, and the reaction mixture was heated to 50°C. Monitoring of the progress of the reaction and isolation of the product proceeded as described above.

1,4-Bis-(1-butyldioxy-1-methylethyl)-benzene (**12**; $C_{20}H_{34}O_4$)

Yield: 88%; n_D^{20}: 1.5264; ^{1}H NMR (CDCl$_3$, δ, 300 MHz): 7.26 (s, 4H, H$_{ar}$), 3.92 (t, $J = 6.6$ Hz, 4H, –O–O–C*H*$_2$–CH$_2$–), 1.59 (s, 12H, Ar–C(CH$_3$)$_2$–O–O–), 1.59–1.50 (m, 4H, –O–O–CH$_2$–C*H*$_2$–CH$_2$–CH$_3$), 1.30–1.26 (m, 4H, –O–O–CH$_2$–CH$_2$–C*H*$_2$–CH$_3$), 0.86 (t, $J = 7.3$ Hz, 6H, –O–O–CH$_2$–CH$_2$–CH$_2$–C*H*$_3$) ppm; ^{13}C NMR (CDCl$_3$, δ, 75 MHz): 144.1, 125.2 (C$_{ar}$), 82.6 (–*C*(CH$_3$)$_2$–O–O–), 74.7 (–O–O–*C*H$_2$–CH$_2$–CH$_2$–CH$_3$), 29.9 (–O–O–CH$_2$–*C*H$_2$–CH$_2$–CH$_3$), 26.5 (–C(*C*H$_3$)$_2$–O–O–), 19.3, 13.9 (–O–O–CH$_2$–CH$_2$–CH$_2$–*C*H$_3$) ppm.

1,4-Bis-(benzyldioxy-1-methylethyl)-benzene (**13**; $C_{26}H_{30}O_4$)

Yield: 82%; m.p.: 48–51°C; ^{1}H NMR (CDCl$_3$, δ, 300 MHz): 7.43 (s, 4H, H$_{ar}$), 7.24–7.29 (m, 10H, H$_{ar}$), 4.90 (s, 4H, –O–O–CH$_2$–Ph), 1.58 (s, 12H, Ar–C(CH$_3$)$_2$–O–O–) ppm; ^{13}C NMR (CDCl$_3$, δ, 75 MHz): 144.0, 135.9, 129.0, 128.2, 128.1, 125.3 (C$_{ar}$), 82.9 (–*C*(CH$_3$)$_2$–O–O–), 77.1 (–O–O–CH$_2$–Ph), 26.5 (–C(*C*H$_3$)$_2$–O–O–) ppm.

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