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Mild Conditions Synthesis of Mixed Organic Peroxides from Alkyl Halides and Organic Hydroperoxides

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The synthesis of mixed organic peroxides by reaction of alkyl halides with tertiary hydroperoxides under basic phase-transfer catalysis conditions was described.

Key words: dialkyl peroxides, hydroperoxides, alkyl halides, alkylation, phase-transfer catalysis

Organic peroxides are subject of continuous interest. These substances have practical application as initiators of free radical reactions [1] and as organic synthesis reagents [2]. The mixed organic peroxides can be obtained as a result of the reaction of organic hydroperoxides and alkyl halides [3–5] in the presence of strong bases. However, such bases can promote, to the significant degree, decomposition of hydroperoxides and peroxides [1,6,7]. Phase-transfer catalysis (PTC) was found to be useful in such synthesis [8–11]. In the previous studies [12–13], we have presented an efficient synthesis of peroxyesters from alkyl hydroperoxides and acyl halides under PTC conditions. The reactions were carried out in a liquid-liquid system (aqueous solution of sodium carbonate, solution of hydroperoxide and acylating agent in hexane) and a liquid-solid system (solid sodium carbonate and solution of reagents in hexane). Moreover, we practically did not notice decomposition of the formed peroxyesters. It was especially interesting that the reaction of synthesis of peroxyesters in the presence of Na_2CO_3 proceeded even when the concentration of ROO^- ion in aqueous phase was low. The low concentration of peroxide anion was caused by lower acidity of cumyl hydroperoxide than carbonate acid (pKa of selected hydroperoxides vary from 11.5 to 13.1 [14] (pKa_1 of H_2CO_3 = 6.3; pKa_2 = 10.3 [15]). It could have been predicted that a similar reaction to obtain mixed organic peroxides is much harder to achieve because alkyl halides are much less reactive than acyl halides. It should be also mentioned that only tertiary hydroperoxides are stable enough to be used as safe and stable reagents.

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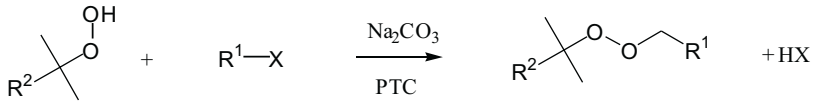
RESULTS AND DISCUSSION

The influence of the composition of the reaction mixture on the reaction course was investigated to optimize reaction conditions. The reaction in the presence of aqueous solution of K_2CO_3 was slightly faster than analogous reaction in presence of Na_2CO_3. Unfortunately, resulting dialkyl peroxides appear to be unstable in the presence of K_2CO_3 and formed decomposition products. The solvent effect was investigated using the most common solvents. The best yield was obtained when cyclohexane or hexane were used. We concluded that amount of water has a significant effect on the yield of peroxide and the reaction rate. The reaction was very slow when anhydrous carbonate was used and accelerated when water was added. Concentrated aqueous solution of Na_2CO_3 could be used as well.

Alkylation of hydroperoxides is relatively slow process in the presence of alkali metal carbonates. However, formed dialkyl peroxides are stable enough under conditions we used and their synthesis can be carried out at higher temperature not exceeding 70°C.

Scheme 1



X	R^1	R^2	Temp (°C)	Yield (%)	Time [h]
Cl	4-chlorobenzyl	Ph	50	21	8
Br	4-bromobenzyl	Ph	50	59	7
Cl	4-methoxybenzyl	Ph	50	55	8
Cl	3-methylbenzyl	Ph	60	35	8
Cl	2-methylbenzyl	Ph	60	58	8
Cl	4-methylbenzyl	Ph	60	25	7
Br	4-*tert*-butylbenzyl	Ph	60	76	6
Br	4-carbonylmethoxybenzyl	Ph	20	65	6
Br	benzyl	Ph	60	62	6
Cl	benzyl	Ph	60	18	8
Br	benzyl	Me	60	51	6
Br	butyl	Ph	50	35	6
Br	propyl	Ph	50	33	6
Br	allyl	Ph	50	51	6

Elaborated procedure is convenient for peroxides which are unstable in the presence of strong bases, especially for benzylic peroxides. Relatively high thermal stability of mixed organic peroxides allows to conduct the reaction in a relatively short time at higher temperatures. Week basic environment allows to avoid decomposition of reagents. Therefore post-reaction mixtures contain very small amounts of by-products. Reactions were conducted until maximum concentration of peroxides was rea-

ched and yields of peroxides are only affected by the degree of halides conversion. Decomposition of alkyl peroxides during purification was not observed. Rates of the reactions of all investigated halides with hydroperoxides in presence of Na_2CO_3 are lower than the corresponding rates in presence of NaOH [11].

This method can be also use for the synthesis of allyl, primary and secondary alkyl peroxides from corresponding halides. In this case yields was lower than yields obtained from the reaction of sodium alkyl peroxide [11] or hydroperoxide–NaOH system [9,10]. This was caused by low reactivity of alkyl halides in investigated reaction conditions.

EXPERIMENTAL

HPLC was performed on a liquid chromatograph (Alliance, Waters 2690 system) with a Waters PDA detector and cartridge column (Merck LichroCART 250-2, Purospher STAR RP-18 5μm); solvent system included acetonitrile-water (90:10, flow 0.25 $cm^3 \cdot min^{-1}$). ^1H and ^{13}C NMR spectra were recorded at 300 MHz in $CDCl_3$ (Varian Unity Inova plus, internal TMS). Mass spectra were recorded on a Waters TMB mass detector; all new compounds gave satisfactory elemental analyses within $\pm 0.4\%$.

Synthesis of dialkyl peroxides (General procedure). Into 100 cm^3 three-necked flask, equipped with a mechanical stirrer and condenser placed in water bath, 0.006 mol of alkyl halide and 0.007 mol of hydroperoxide dissolved in 40 cm^3 of hexane, 0.4 g tetrabutylammonium bromide, 5 g Na_2CO_3 and 10 g H_2O were added. The reaction was conducted in 20–60°C for 6–8 h with vigorous strirring. The reaction course was controlled using the HPLC. After the reaction was completed the organic layer was washed with water, dried over anhydrous $MgSO_4$ and concentrated. Crude product was purified using the column chromatography with toluene. In case of 4-(methoxycarbonyl)benzyl 1-methyl-1-phenylethyl peroxide hexane:acetone (98:2) was used as an eluent. Pure peroxides were obtained after evaporation of solvent under vacuum at 30°C. In case of 4-chlorobenzyl 1-methyl-1-phenylethyl peroxide, 4-bromobenzyl 1-methyl-1-phenylethyl peroxide, 4-methoxybenzyl 1-methyl-1-phenylethyl peroxide and 4-(methoxycarbonyl)benzyl 1-methyl-1-phenylethyl peroxide after chromatography products were crystallized from hexane. The following compounds were obtained:

4-Chlorobenzyl 1-methyl-1-phenylethyl peroxide. Colorless crystals, m.p. 48–49°C, Anal. Calcd. for $C_{16}H_{17}O_2Cl$: C, 69.4; H, 6.2. Found: C, 69.7; H, 6.1; ^1H NMR: δ 1.56 (s, 6H), 4.84 (s, 2H), 7.19–7.44 (m, 9H); ^{13}C NMR: δ 26.48, 76.19, 83.09, 125.56, 127.16, 128.03, 128.43, 130.24, 133.92, 134.83, 145.13; MS (70 eV, EI): m/z (%): 119 (100), 77 (40), 121 (30), 91 (26), 51 (16), 79 (15), 118 (14), 105 (13), 120 (12), 142 (12), 107 (12), 117 (11), 139 (11), 78 (11), 111 (9), 103 (8).

4-Bromobenzyl 1-methyl-1-phenylethyl peroxide. Colorless crystals, m.p. 54–55°C. Anal. Calcd. for $C_{16}H_{17}O_2Br$: C, 59.8; H, 5.3. Found: C, 59.9; H, 5.4; ^1H NMR: δ 1.56 (s, 6H), 4.81 (s, 2H), 7.10–7.46 (m, 9H); ^{13}C NMR: δ 26.47, 76.21, 83.09, 122.09, 125.54, 127.15, 128.02, 130.53, 131.38, 135.36, 145.10; MS (70 eV, EI): m/z (%): 119 (100), 77 (52), 121 (41), 91 (39), 118 (27), 79 (26), 51 (25), 117 (23), 78 (23), 105 (23), 186 (17), 107 (16), 103 (16), 185 (13), 120 (12), 183 (12).

4-Methoxybenzyl 1-methyl-1-phenylethyl peroxide. Colorless crystals, m.p. 44–45°C. Anal. Calcd. for $C_{17}H_{20}O_3$: C, 75.0; H, 7.4. Found: C, 75.3; H, 7.8; ^1H NMR: δ 1.60 (s, 6H), 3.80 (s, 3H), 4.84 (s, 2H) 6.84–7.50 (m, 9H); ^{13}C NMR: δ 26.50, 55.21, 76.73, 82.94, 113.64, 125.62, 127.06, 127.98, 130.75, 145.27, 159.58; MS (70 eV, EI): m/z (%): 121 (100), 77 (43), 119 (42), 118 (25), 91 (24), 117 (21), 122 (20), 135 (20), 78 (19), 105 (18), 51 (17), 136 (14), 103 (13), 138 (11), 107 (11), 109 (10).

3-Methylbenzyl 1-methyl-1-phenylethyl peroxide. Colorless oil. Anal. Calcd. for $C_{17}H_{20}O_3$: C, 79.7; H, 7.9. Found: C, 79.9; H, 8.1; ^1H NMR: δ 1.60 (s, 6H), 2.32 (s, 3H), 4.86 (s, 2H), 7.05–7.47 (m, 9H); ^{13}C NMR: δ 21.30, 26.51, 77.18, 83.02, 125.62, 126.08, 127.07, 127.98, 128.14, 128.86, 129.77, 135.89, 137.85, 145.28; MS (70 eV, EI): m/z (%): 119 (100), 91 (40), 121 (25), 77 (21), 105 (15), 122 (12), 120 (11), 107 (9), 118 (9), 79 (8), 51 (8), 65 (8), 78 (7), 117 (7), 103 (7), 93 (5).

2-Methylbenzyl 1-methyl-1-phenylethyl peroxide. Colorless oil. Anal. Calcd. for $C_{17}H_{20}O_3$: C, 79.7; H, 7.9. Found: C, 79.8; H, 7.8; ^{1}H NMR: δ 1.58 (s, 6H), 2.19 (s, 3H), 4.92 (s, 2H), 7.12–7.49 (m, 9H); ^{13}C NMR: δ 18.77, 26.54, 75.12, 82.86, 125.59, 125.70, 127.04, 127.97, 128.45, 130.14, 130.49, 133.73, 137.77, 145.40; MS (70 eV, EI): m/z (%): 119 (100), 91 (40), 121 (23), 77 (22), 105 (17), 104 (15), 120 (13), 78 (9), 118 (9), 51 (9), 79 (9), 103 (8), 65 (8), 117 (8), 122 (5), 107 (5).

4-Methylbenzyl 1-methyl-1-phenylethyl peroxide. Colorless oil. Anal. Calcd. for $C_{17}H_{20}O_3$: C, 79.7; H, 7.9. Found: C, 79.6; H, 7.7; ^{1}H NMR: δ 1.58 (s, 6H), 2.32 (s, 3H), 4.85 (s, 2H), 7.12–7.49 (m, 9H); ^{13}C NMR: δ 21.11, 26.52, 82.99, 125.62, 127.07, 127.99, 128.96, 129.15, 132.96, 137.92, 145.32; MS (70 eV, EI): m/z (%): 119 (100), 91 (46), 121 (25), 77 (22), 105 (18), 122 (12), 107 (11), 120 (11), 118 (10), 51 (10), 79 (10), 78 (8), 65 (8), 117 (8), 103 (7), 93 (5).

4-*tert*-Butylbenzyl 1-methyl-1-phenylethyl peroxide. Colorless oil. Anal. Calcd. for $C_{20}H_{26}O_2$: C, 80.5; H, 8.8. Found: C, 80.3; H, 8.6; ^{1}H NMR: δ 1.30 (s, 9H), 1.60 (s, 6H), 4.87 (s, 2H), 7.17–7.49 (m, 9H); ^{13}C NMR: δ 26.52, 31.31, 34.54, 76.93, 83.04, 125.21, 125.63, 127.06, 127.98, 128.87, 132.86, 145.30, 151.12; MS (70 eV, EI): m/z (%): 119 (100), 91 (45), 149 (43), 121 (34), 147 (29), 77 (27), 105 (23), 118 (23), 117 (23), 103 14), 51 (14), 133 (13), 78 (13), 120 (13), 115 (13), 164 (9).

4-(Methoxycarbonyl)benzyl 1-methyl-1-phenylethyl peroxide. Colorless crystals, m.p. 43–44°C. Anal. Calcd. for $C_{18}H_{20}O_4$: C, 72.0; H, 6.7. Found: C, 72.1; H, 6.8; ,^{1}H NMR: δ 1.57 (s, 6H), 3,91 (s, 3H), 4.94 (s, 2H), 7.32–8.01 (m, 9H); ^{13}C NMR: δ 26.49, 52.06, 76.33, 83.17, 125.52, 127.16, 128.04, 128.40, 129.55, 129.71, 141.71, 145.11, 166.89; MS (70 eV, EI): m/z (%): 119 (100), 121 (33), 77 (33), 133 (25), 91 (24), 105 (24), 51 (16), 164 (14), 135 (14), 118 13), 120 (13), 107 (12), 78 (11), 117 (10), 103 (9), 79 (8).

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