ISSN 1070-3632, Russian Journal of General Chemistry, 2011, Vol. 81, No. 11, pp. 2379–2380. © Pleiades Publishing, Ltd., 2011.
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LETTERS TO THE EDITOR

Synthesis of Acrylates and Methacrylates Based on *tert*-Butylperoxy-α-Chloroalkoxyethanes

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Received June 16, 2011

DOI: 10.1134/S1070363211110302

Peroxide monomers are used as initiators of free radical processes and for the synthesis of modified copolymer having a complex of valuable properties [1]. The use of peroxide initiators with the (meth) acrylate fragments, α-located relative to peroxide group, is limited because of their lability, explosivity and spontaneous polymerization [1].

To obtain the peroxy acetal-acylals with the peroxide group separated from acrylate or methacrylate fragments we performed the nucleophilic substitution of chlorine in the α-chloroethers on the basis of 2-*tert*-butylperoxyethanol [2], with the retention of O–O bond [3].

$$(CH_3)_3COOCH_2CH_2OCH(R^1)Cl + R^2COONa$$

$$\rightarrow (CH_3)_3COOCH_2CH_2OCH(R^1)OC(O)R^2 + NaCl,$$

$R^1 = H$, $R^2 = CH_2{=}CH$ (**I**); $R^1 = CH_3$, $R^2 = CH_2{=}CH$ (**II**); $R^1 = C_2H_5$, $R^2 = CH_2{=}CH$ (**III**); $R^1 = H$, $R^2 = CH_2{=}C(CH_3)$ (**IV**); $R^1 = CH_3$, $R^2 = CH_2{=}C(CH_3)$ (**V**).

The reaction was carried out in *n*-hexane medium at 40–45°C for 4–4.5 h (yield 43–62%). A high yield of the target products is due to the reaction proceeding in heterophase. When using polar solvents, the reaction is complicated by the processes of thermal decomposition of the initial α-chloroethers in the presence of acid salts.

The individuality of peroxides **I**–**V** was confirmed by TLC. Their structure was confirmed by the IR spectroscopy, the composition, by the elemental analysis data and active oxygen determination. The synthesized peroxides are colorless liquids, very soluble in organic solvents and insoluble in water. They liberate readily iodine from the acidified potassium iodide solution, whereas the do not change the percentage of active oxygen at 4–8°C for 30–45 days, i.e., they are more stable compared with the known peroxide monomers [1].

1-*tert*-Butylperoxy-2-(acryloyloxymethoxy)ethane (I). To 18.25 g (0.10 mol) of 1-*tert*-butylperoxy-2-chloromethoxyethane in 200 ml of hexane was added 9.4 g (0.10 mol) of sodium acrylate. The mixture was kept under stirring at 40–45°C for 4–4.5 h. The precipitated salt was filtered off, the hexane solution was washed with 10% sodium bicarbonate solution and water until a neutral reaction, dried over magnesium sulfate and passed through a layer of aluminum oxide of II activity degree. Hexane was removed under reduced pressure, and the residue was kept in vacuum of 1.33 GPa at room temperature for 1–2 h. Yield 10.9–11.2 g (50–51%), n_D^{20} 1.4316, d_4^{20} 1.0232, MR_D 55.20 (calculated 55.04). R_f 0.46 (diethyl ether–hexane, 1:4). IR spectrum, ν, cm^{-1}: 874 (O–O), 1732 (C=O), 1642 (C=C), 1050 (C–O–O–C). Found, %: O_{act} 7.41, 7.48; C 55.04, 55.06; H 8.27, 8.26. $C_{10}H_{18}O_5$. Calculated, %: O_{act} 7.34; C 55.05; H 8.25.

1-*tert*-Butylperoxy-2[1'-(acryloyloxy)ethoxy]ethane (II) was prepared similarly from 9.83 g (0.05 mol) 1-*tert*-butylperoxy-2-(1'-chloroethoxy)ethane and 4.7 g (0.05 mol) of sodium acrylate in 100 ml of hexane. Yield 6.50–6.73 g (56–58%), n_D^{20} 1.4300, d_4^{20} 1.0081, MR_D 59.46 (calculated 59.66). R_f 0.48 (diethyl ether–hexane, 1:4). IR spectrum, ν, cm^{-1}: 872 (O–O), 1732 (C=O), 1642 (C=C), 1048 (C–O–O–C). Found, %: O_{act} 6.85, 6.83; C 56.66, 56.79; H 8.72, 8.68. $C_{11}H_{20}O_5$. Calculated, %: O_{act} 6.89; C 56.89; H 8.62.

1-*tert*-Butylperoxy-2-[1'-(acryloyloxy)propoxy]-ethane (III) was prepared similarly from 5.26 g (0.025 mol) 1-*tert*-butylperoxy-2-(1'-chloroethoxy)-

ethane and 2.25 g (0.025 mol) of sodium acrylates in 50 ml of hexane. Yield 2.58–2.64 g (42–43%), n_D^{20} 1.4320, d_4^{20} 0.9936, MR_D 64.29 (calculated 64.28). R_f 0.50 (diethyl ether–hexane, 1:4). IR spectrum, ν, cm^{-1}: 872 (O–O), 1729 (C=O), 1640 (C=C), 1050 (C–O–O–C). Found, %: O_{act} 6.45, 6.48; C 58.35, 58.45; H 9.00, 8.98. $C_{12}H_{22}O_5$. Calculated, %: O_{act} 6.50; C 58.54; H 8.94.

1-*tert*-Butylperoxy-2-(methacryloyloxymethoxy)-ethane (IV) was prepared similary from 18.25 g (0.10 mol) 1-*tert*-butylperoxy-2-chloromethoxyethane and 10.8 g (0.10 mol) of sodium methacrylate 200 ml of hexane. Yield 12.5–12.7 g (54–55%), n_D^{20} 1.4366, d_4^{20} 1.0149, MR_D 59.64 (calculated 59.66). R_f 0.54 (diethyl ether–hexane, 1:4). IR spectrum, ν, cm^{-1}: 875 (O–O), 1732 (C=O), 1642 (C=C), 1053 (C–O–O–C). Found, %: O_{act} 6.86, 6.88; C 58.66, 58.75; H 8.53, 8.56. $C_{11}H_{20}O_5$. Calculated, %: O_{act} 6.89; C 58.89; H 8.62.

1-*tert*-Butylperoxy-2-[1'-(methacryloxy)ethoxy]-ethane (V) was prepared similarly from 7.86 g (0.04 mol) of 1-*tert*-butylperoxy-2-(1'-chloroethoxy)-ethane and 4.32 g (0.04 mol) of sodium methacrylate in 80 ml of hexane. Yield 6.0–6.1 g (61–62%), n_D^{20} 1.4308, d_4^{20} 0.9857, MR_D 64.56 (calculated 64.36). R_f 0.56 (diethyl ether–hexane, 1:4). IR spectrum, ν, cm^{-1}: 872 (O–O), 1730 (C=O), 1640 (C=C), 1053 (C–O–O–C). Found, %: O_{act} 6.45, 6.47; C 58.36, 58.44; H 8.80, 8.83. $C_{12}H_{22}O_5$. Calculated, %: O_{act} 6.50; C 58.54; H 8.94.

IR spectra were recorded on a Specord M-82 instrument. The active oxygen content was determined by the procedure [4].

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