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LETTERS TO THE EDITOR

Synthesis of α-*tert*-Butylperoxyethyl Perfluorocarboxylates

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α-Chloroalkyl-*tert*-butylperoxides react with alcohols to form *tert*-butylperoxy ethers, the initiators of monomers polymerization and rubber vulcanization [1].

We synthesized some α-*tert*-butylperoxyethyl perfluoroalkylcarboxylates by reaction of α-chloroethyl-*tert*-butylperoxide **I** with silver perfluorocarboxylates:

$$(CH_3)_3COOCH(CH_3)Cl + R_FC(O)OAg \rightarrow (CH_3)_3COOCH(CH_3)OC(O)R_F,$$
II–VI

$R_F = CF_3$ (**II**), $CF_3(CF_2)_2$ (**III**), $CF_3(CF_2)_3$ (**IV**), $CF_3(CF_2)_5$ (**V**), $CF_3OCF_2CF_2$ (**VI**).

Reaction was carried out in hexane, Freon-113, chloroform, diethyl ether. The perfluorinated esters yields were 44.5–65%. Better yields were obtained in polar diethyl ether.

Nucleophilic substitution of α-chloroperoxides and α-chloroesters in polar media proceeds more readily due to S_N1 substitution mechanism. This mechanism is proved by correlation of the first order rate constants of hydrolysis in 87.65% dioxane and 12.35% water with the positive charge ΣQ compensation in carbocation of general formula $ROCH_2^+$, where R = CH_3, OCH_2Cl, OCH_3 [2,3].

α-*tert*-Butylperoxyethyl perfluoroacetate (II). To a solution of 0.04 mol (8.8 g) of silver trifluoroacetate (silver perfluorocarboxylate was prepared by the reaction of the corresponding perfluorocarboxylic acids with silver oxide [5]) in 60 ml of dry ether was added 0.04 mol (6.4 g) of the freshly distilled α-chloroethyl-*tert*-butylperoxide at 0 to 5°C. Then temperature was gradually increased. The reaction mixture was stirred at 25–35°C for 3–4 h. Silver chloride precipitate was filtered off. The organic mass was washed rapidly with sodium hydrogen carbonate solution and water to neutral reaction. After the solvent removal the residue was distilled in a vacuum. Yield 65%, bp 27.5–28°C (7 mm Hg), d_4^{20} 1.1703, n_D^{20} 1.3650. Found, %: C 41.98; H 5.60; O_{act} 7.05; MR_D 43.91. $C_8H_{13}O_4F_3$. Calculated, %: C 41.73; H 5.65; O_{act} 6.96; MR_D 43.89.

α-*tert*-Butylperoxyethyl perfluorobutyrate (III). Yield 54.5%, bp 40–42°C (7 mm Hg), d_4^{20} 1.3763, n_D^{20} 1.3561. Found, %: C 37.2; H 3.85; O_{act} 4.81; MR_D 56.69. $C_9H_{13}O_4F_7$. Calculated, %: C 36.36; H 3.94; O_{act} 4.85; MR_D 52.30.

α-*tert*-Butylperoxyethyl perfluorovalerianate (IV). Yield 57%, bp 36.5–37°C (1.5 mm Hg), d_4^{20} 1.4560, n_D^{20} 1.3530. MR_D 56.69, calculated 56.57. Found, %: C 33.7; H 3.84; O_{act} 3.25. $C_{11}H_{13}O_4F_9$. Calculated, %: C 34.66; H 2.71; O_{act} 3.33.

α-*tert*-Butylperoxyethyl perfluoroheptanate (V). Yield 57.8 %, bp 67.5–65.2°C (2 mm Hg), d_4^{20} 1.5645, n_D^{20} 1.3445. Found, %: C 33.00; H 3.70; O_{act} 4.30; MR_D 63.08. $C_{13}H_{13}O_4F_{13}$. Calculated, %: C 32.5; H 3.85; O_{act} 4.39; MR_D 62.93.

α-*tert*-Butylperoxyethyl perfluoromethoxybutyrate (VI). Yield 44.5%, bp 40.5–41°C (13 mm Hg), d_4^{20} 1.3744, n_D^{20} 1.3495. Found, %: C 34.64; H 3.73; O_{act} 4.52; MR_D 52.10. $C_{10}H_{13}F_7O_5$. Calculated, %: C 34.68; H 3.76; O_{act} 4.62; MR_D 54.06.

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