

New Synthesis of *tert*-Butyl Peroxycarboxylates

V. A. Donchak, S. A. Voronov, and R. S. Yur'ev

L'vovskaya Politekhnikha National University, ul. S. Bandery 12, L'vov, 79013 Ukraine
e-mail: donchak@polynet.lviv.ua

Received March 27, 2004

Abstract—*tert*-Butyl peroxyacetate, *tert*-butyl peroxybutyrate, *tert*-butyl phenylperoxyacetate, and *tert*-butyl peroxyundecanoate were obtained in nearly quantitative yields by the esterification of the corresponding carboxylic acids with *tert*-butyl hydroperoxide in the presence of trifluoroacetic anhydride and pyridine in nonaqueous medium at 0–5°C. No *tert*-butyl peroxytrifluoroacetate was formed as a by-product during the process. A possible reaction mechanism is discussed.

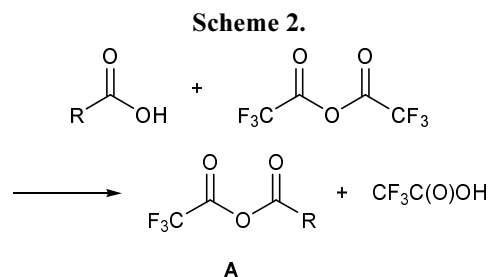
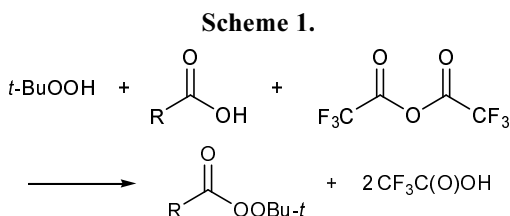
DOI: 10.1134/S1070428006040026

Peroxycarboxylic acid esters are used in chemical technology as effective radical initiators [1, 2] due to their ability to undergo homolytic dissociation with the formation of two radical species possessing different reactivities.

Known methods of synthesis of peroxy esters are based on acylation of hydroperoxides with appropriate acylating agents, such as carboxylic acid halides [3] and anhydrides [4]; in some cases, carboxylic acids themselves may be used [5, 6]. Among the above listed acylating agents, the most accessible are carboxylic acids. They are capable of acylating hydroperoxides in the presence of strong mineral acids. This procedure requires no preliminary transformation of carboxylic acid into some acylating agent. However, its synthetic potential is restricted due to the necessity of using relatively large concentrations of mineral acids. The reaction is reversible; therefore, dehydrating agents (such as anhydrous Na₂SO₄, MgSO₄, or B₂O₃) are usually added to increase the conversion. Nevertheless, satisfactory yields are obtained only in the acylation of *tert*-butyl and *tert*-pentyl hydroperoxides with lower fatty acids [6]. Acylation of hydroperoxides with carboxylic acids can also be effected in the presence of imidazole [7]. In this case, the yields of peroxy esters reach 60–80%, but the reaction is accompanied by side

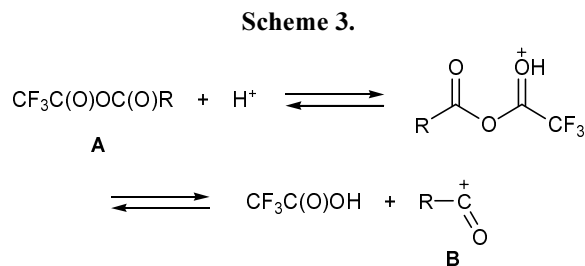
processes, and the products are difficult to purify. Furthermore, high cost of imidazoles prevents wide application of this procedure in chemical technology.

In the present work we showed that peroxy esters can be synthesized by acylation of *tert*-butyl hydroperoxides with aliphatic carboxylic acids in nonaqueous medium in the presence of trifluoroacetic anhydride (TFA) (Scheme 1). It is known that alcohols react with carboxylic acids in the presence of TFA under mild conditions to give the corresponding esters in one step in nearly quantitative yield [8]. High yields were obtained even in the acylation of sterically hindered alcohols and phenols. While studying the reaction mechanism, Parish and Stock [8] concluded that carboxylic acids react with TFA to form mixed anhydride **A** which is characterized by enhanced acylating power (Scheme 2).

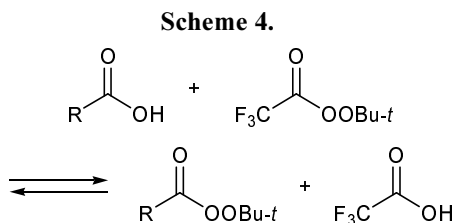


Nucleophilic attack is directed mainly at the carbonyl carbon atom linked to the alkyl rather than trifluoromethyl group; as a result, the corresponding carboxylic rather than trifluoroacetic acid ester is formed. Also, the possibility for formation of acylium ion **B** via protonation of mixed anhydride and sub-

sequent elimination of trifluoroacetic acid cannot be ruled out (Scheme 3).



It was surprising that the acylation of *tert*-butyl hydroperoxide with acetic, butyric, and undecanoic acids in the presence of TFA afforded no more than 50% of the corresponding esters. Moreover, the yield of peroxy esters considerably decreased as the ratio TFA–carboxylic acid increased. A probable reason is that strong trifluoroacetic acid protonates *tert*-butyl hydroperoxide which is a stronger base than alcohols. Being a weak nucleophile, protonated hydroperoxide is incapable of reacting with mixed anhydride **A** or acylium ion **B** to produce the corresponding peroxy ester. Protonation of *tert*-butyl hydroperoxide may be avoided by adding a stronger proton acceptor, e.g., pyridine, to the reaction mixture. Pyridine reduces the acidity of the medium, thus hampering undesirable decomposition of peroxides. On the other hand, it enhances the reactivity of mixed anhydride **A** due to formation of charge-transfer complex [9]. All these factors favor increased yield of peroxy esters. At a pyridine-to-TFA ratio of 2:1, peroxy esters were formed in almost quantitative yield in 1 h at 0–5°C, and no *tert*-butyl trifluoroperoxyacetate was detected. This means that under the given conditions *tert*-butyl hydroperoxide reacts predominantly with mixed anhydride **A** rather than with TFA, as it was observed previously [8] in the acylation of weaker nucleophiles (alcohols); however, the formation of peroxy esters as a result of thermodynamically controlled transesterification process cannot be excluded (Scheme 4).



It is advisable to use excess of carboxylic acid and trifluoroacetic anhydride in the synthesis of peroxy

esters. In this case, *tert*-butyl hydroperoxide is consumed almost completely, and excess acids are readily separated from the target product by washing with an aqueous solution of sodium hydrogen carbonate. The acylation of hydroperoxides with carboxylic acids in the presence of TFA can be performed both in a non-aqueous solvent and without it. In any case, the reaction mixture should be maintained at 0–5°C to avoid decomposition of peroxy compounds due to evolution of heat during the process. The most appropriate solvents are chlorinated hydrocarbons (chloroform, 1,2-dichloroethane) and aromatic hydrocarbons (benzene, toluene) which ensure homogeneous reaction mixture. The results of acylation of *tert*-butyl hydroperoxide in the presence of TFA (method *a*) and in the presence of TFA and pyridine (method *b*) are collected in table.

Thus we have demonstrated the possibility for synthesizing peroxy esters by acylation of *tert*-butyl hydroperoxide with aliphatic carboxylic acids in the presence of trifluoroacetic anhydride and pyridine. The products are formed in almost quantitative yield, and the reaction is not accompanied by side processes leading to other peroxy compounds.

EXPERIMENTAL

Acetic, butyric, undecanoic, and phenylacetic acids and trifluoroacetic anhydride of analytical grade were used without additional purification. Benzene, toluene, chloroform, 1,2-dichloroethane, and pyridine were purified by the procedures described in [10]. *tert*-Butyl hydroperoxide was prepared by reaction of hydrogen peroxide with *tert*-butyl alcohol as reported in [11] and was purified by vacuum distillation at 15 mm; $n_D^{20} = 1.4011$; published data [11]: $n_D^{20} = 1.4013$; concentration of active oxygen 17.6% (calculated 17.7%).

Thin-layer chromatography was performed on Silufol UV-254 plates using toluene–1,2-dichloroethane (1:1) as eluent; the chromatograms were treated with a solution of *N,N*-dimethyl-*p*-phenylenediamine hydrochloride as a reagent selective for peroxy compounds [12]. The isolated peroxy esters were identified by comparing with authentic samples which were prepared from the corresponding carboxylic acid chlorides and *tert*-butyl hydroperoxide according to the procedures described in [3]; *tert*-butyl trifluoroperoxyacetate was synthesized by acylation of *tert*-butyl hydroperoxide with trifluoroacetic anhydride in hexane.

Yields, refractive indices, and analytical data of the synthesized peroxy esters

Compound	Solvent	Yield, %		n_D^{20} ^a	Active oxygen, %: found (calculated)	R_f	
		<i>a</i>	<i>b</i>			isolated	authentic
<i>tert</i> -Butyl peroxyacetate	Toluene	47	95	1.4060 (1.4050)	12.0 (12.1)	0.21	0.20
<i>tert</i> -Butyl peroxybutyrate	Chloroform	42	92	1.4155 (1.4153)	10.3 (10.0)	0.27	0.27
<i>tert</i> -Butyl peroxyundecanoate	1,2-Dichloroethane	45	93	1.4350	6.1 (6.2)	0.41	0.40
<i>tert</i> -Butyl phenylperoxyacetate	Toluene	42	93	1.4170	7.5 (7.7)	0.32	0.32

^a Published values [14] are given in parentheses.

Synthesis of *tert*-butyl peroxy-carboxylates (general procedure). *a.* Trifluoroacetic anhydride, 5 mmol, was added under stirring to a solution of 5 mmol of the corresponding carboxylic acid in 5 ml of appropriate solvent. The mixture was stirred for 15 min and cooled to 0–2°C, and 3 mmol of *tert*-butyl hydroperoxide was added dropwise under vigorous stirring at such a rate that the temperature did not exceed 5°C. The mixture was then stirred for 45 min, allowing it to gradually warm up to room temperature.

b. Trifluoroacetic anhydride, 5 mmol, was added under stirring to a solution of 5 mmol of the corresponding carboxylic acid in 5 ml of appropriate solvent, the mixture was cooled to 5°C, and 5 mmol of pyridine was slowly added dropwise under stirring. The mixture was stirred for 15 min and cooled to 0–2°C, 3 mmol of *tert*-butyl hydroperoxide was added dropwise under vigorous stirring, and 5 mmol of pyridine was added dropwise; during the addition of *tert*-butyl hydroperoxide and pyridine, the temperature was maintained below 5°C. The mixture was then stirred for 45 min, allowing it to gradually warm up to room temperature.

When the reaction was complete, the mixture was washed with a saturated aqueous solution of sodium hydrogen carbonate (3×5 ml) to remove excess acids and anhydrides. The solvent was distilled from the organic phase under reduced pressure at a bath temperature not exceeding 50°C, and the residue was distilled under reduced pressure. The products were identified by measuring the concentration of active oxygen, as well as by refractometry and TLC (see table).

To determine the yield, the reaction mixture was washed with water and analyzed for *tert*-butyl hydroperoxide by cerimetry and for peroxy ester by iodometry [13]. The yield (η) was calculated by the formula

$$\eta = c_{PE}/(c_{PE} + c_{TBHP}) \times 100,$$

where c_{PE} is the concentration of peroxy ester, mequiv/g, and c_{TBHP} is the concentration of *tert*-butyl hydroperoxide, mequiv/g.

This study was performed under financial support by the Ukrainian Scientific and Technical Center (project no. 1930).

REFERENCES

1. Rakhimov, A.I., *Khimiya i tekhnologiya organicheskikh perekisnykh soedinenii* (Chemistry and Technology of Organic Peroxy Compounds), Moscow: Khimiya, 1979.
2. Bratichak, M.M. and Sikors'kii, R.T., *Osnovi sintezu i reaktsiinoi zdatnosti visokomolekulyarnikh spoluk* (Principles of Synthesis and Reactivity of High-Molecular Compounds), L'viv: Nats. Univ. L'vivska Politekh., 2003.
3. Bartlett, P.D. and Hiatt, R.R., *J. Am. Chem. Soc.*, 1958, vol. 80, p. 1398; Hock, H., *Chem. Ber.*, 1955, vol. 88, p. 1544; Lorand, O.P. and Bartlett, P.D., *J. Am. Chem. Soc.*, 1966, vol. 88, p. 3294.
4. *Uspekhi khimii organicheskikh perekisnykh soedinenii i autookisleniya* (Advances in the Chemistry of Organic Peroxy Compounds and Autooxidation), Emanuel', N.M., Ed., Moscow: Khimiya, 1969; Pincock, R.E., *J. Am. Chem. Soc.*, 1964, vol. 86, p. 1820; *Khimiya perekisnykh soedinenii* (Chemistry of Peroxy Compounds), Chernyayev, I.I., Ed., Moscow: Akad. Nauk SSSR, 1963; Ol'dekop, Yu.A., Bylina, G.S., and Bulochik, B.I., *Izv. Akad. Nauk BSSR, Ser. Khim.*, 1970, no. 2, p. 109.
5. Ruchardt, Ch. and Hecht, H., *Chem. Ber.*, 1964, vol. 97, p. 2716; Lyashenko, O.K., Nesterova, I.P., and Antonovskii, V.L., *Khim. Promst.*, 1974, no. 9, p. 659; UK Patent no. 1072296, 1967; UK Patent no. 1226468, 1971; Pincock, R.E., *J. Am. Chem. Soc.*, 1965, vol. 87, p. 1274.
6. Antonovskii, V.L. and Lyashenko, O.K., *Zh. Org. Khim.*, 1972, vol. 8, p. 2615.
7. Hecht, R. and Ruchardt, Ch., *Chem. Ber.*, 1963, vol. 96, p. 1281; Staab, H.A., Rohr, W., and Graf, F., *Chem. Ber.*, 1965, vol. 98, p. 1122.

8. Parish, R.C. and Stock, L.M., *J. Org. Chem.*, 1965, vol. 30, p. 65.
9. Zubkov, V.A., Koton, M.M., Kudryavtsev, V.V., and Svetlichnyi, V.M., *Zh. Org. Khim.*, 1980, vol. 16, p. 2486.
10. Weissberger, A., Proskauer, E.S., Riddick, J.A., and Toops, E.E., Jr., *Organic Solvents: Physical Properties and Methods of Purification*, New York: Intersci., 1955, 2nd ed.
11. Milas, N.A. and Surgenor, D., *J. Am. Chem. Soc.*, 1946, vol. 68, p. 642.
12. Perry, S.G., Amos, R., and Brewer, P.I., *Practical Liquid Chromatography*, New York: Plenum, 1972. Translated under the title *Prakticheskoe rukovodstvo po zhidkostnoi khromatografii*, Moscow: Mir, 1974, p. 164.
13. Antonovskii, V.L. and Buzlanova, M.M., *Analiticheskaya khimiya organicheskikh peroksidnykh soedinenii* (Analytical Chemistry of Organic Peroxy Compounds), Moscow: Khimiya, 1978.
14. Antonovskii, V.L., *Organicheskie perekisnye initsiatory* (Organic Peroxide Initiators), Moscow: Khimiya, 1972.