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ORGANIC SYNTHESIS AND INDUSTRIAL ORGANIC CHEMISTRY

Synthesis of α-Hydroxyalkyl Peroxide Esters and Ethers as Initiators of Radical Processes

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Abstract—α-Hydroxyalkyl peroxide esters and ethers containing, along with the peroxy bond, also acyloxy and alkoxy groups, are effective initiators of radical processes. The initiation efficiency is due to the capability of these molecules to generate simultaneously oxygen- and carbon-centered radicals capable of hydrogen abstraction from the substrate and of addition to >C=C< bonds. The selectivity of the synthesis of α-hydroxyalkyl peroxide esters and ethers is mainly determined by the steps of the synthesis and isolation of the intermediate α-chloroalkyl peroxides, because of their high reactivity. Experimental conditions allowing control of the synthesis of α-hydroxyalkyl peroxide esters and ethers were found.

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α-Hydroxyalkyl peroxide (OP) esters and ethers containing, along with the O–O bond, also alkoxy and acyloxy groups are effective initiators of radical processes: (co)polymerization [1, 2], vulcanization, addition to multiple bonds [3], and substitution of C–H bonds [4]; they are also used as comonomers in copolymerization with nonperoxy monomers [1, 5] and in polymer compounds [1, 6–10]. The polyfunctionality of these molecules is responsible for their ability to generate both oxygen-centered radicals, abstracting hydrogen from a substrate in most cases, and carbon-centered alkyl radicals, undergoing addition to multiple bonds. Owing to this ability, OP esters and ethers find diverse applications as initiators of radical processes.

Thermal decomposition of OP esters (ethers) apparently occurs by the mechanism of concerted cleavage of two bonds, peroxy and ester (ether) bonds, with the formation of tert-butoxy and acetyl radicals and of the corresponding carboxylic acids [11, 12]

$$(CH_3)_3COOCH(CH_3)OC(O)R \longrightarrow (CH_3)_3CO^{\bullet} + CH_3CO^{\bullet} + RC(O)OH$$

or alcohols

$$(CH_3)_3COOCH(CH_3)OR \longrightarrow (CH_3)_3CO^{\bullet} + CH_3CO^{\bullet} + ROH.$$

The generated *tert*-butoxy radical abstracts the hydrogen atom from the substrate to form *tert*-butanol (TB) or decomposes to acetone and methyl radical:

$$(CH_3)_3CO^{\bullet} \xrightarrow{RH} (CH_3)_3COH + R^{\bullet},$$
$$(CH_3)_3CO^{\bullet} \longrightarrow (CH_3)_2CO + CH_3^{\bullet}.$$

The acetyl radicals undergo decarbonylation to form methyl radicals:

$$CH_3CO^{\bullet} \longrightarrow CH_3^{\bullet} + CO.$$

The use of these initiators in radical processes is restricted by the lack of technology for their production. The synthesis methods described in the literature [6, 9, 13] are preparative and multistep; the synthesis is complicated by high reactivity and instability of the starting compounds, intermediates, and target products.

From the technological viewpoint, the most promising route to these initiators is the reaction of α-chloroalkyl

peroxides (CPs) with alcohols and complexes of trialkylamines with carboxylic acids. However, CPs themselves, prone to diverse chemical transformations, are studied insufficiently. This particularly concerns methods of their synthesis.

This study was aimed at finding experimental conditions allowing control of the reactions of CP synthesis and transformation into OP esters and ethers.

SYNTHESIS OF CPs

It is known [14, 15] that CPs are synthesized by the replacement of hemiacetal hydroxyl in OP by chlorine under the action of excess HCl in the presence of a solvent. Because OPs dissociate into the starting compounds on heating, they are hydrochlorinated without isolation from the reaction mixture:

$$(CH_3)_3COOH + RCHO + HCl \longrightarrow (CH_3)_3COOCH(R)Cl + H_2O, \quad (1)$$

where R = Me, Et, Pr, *i*-Pr.

Reaction (1) is not selective. Along with CP, symmetrical di-*tert*-butylperoxy acetal (DP) is formed; it is difficult to separate it from the target peroxide because of their close boiling points:

$$2(CH_3)_3COOH + RCHO \xrightarrow{H^+} (CH_3)_3COOCH(R)OOC(CH_3)_3 + H_2O.$$

Synthesis of CPs via OPs. Synthesis of CPs in the presence of a solvent seems promising. This fact stimulated us to study in more detail reaction (1) as the basis of the future industrial process. Synthesis of CPs by reaction (1) can be described by a more detailed scheme:

$$(CH_3)_3COOH + RCHO \underset{H_2O}{\overset{H^+}{\rightleftharpoons}} (CH_3)_3COOCH(R)OH \rightleftharpoons [(CH_3)_3COO\overset{+}{C}H(R)] \xrightarrow{HCl} (CH_3)_3COOCH(R)Cl, \quad \xrightarrow{(CH_3)_3COOH} (CH_3)_3COOCH(R)OOC(CH_3)_3. \quad (2)$$

It evidently follows from scheme (2) that the reaction is complex and that an OP, transforming in acid solution into a carbocation, is necessarily formed as intermediate. Specifically the reactions of the carbocation determine the selectivity of the whole process, because this substrate can "choose" the pathways of further transformations, reacting either with HCl or with hydroperoxide (HP). Synthesis of a CP under definite conditions always yields DP as by-product along with the target product.

Analysis of scheme (2) from the viewpoint of optimization of the CP yield and selectivity allows making apparent assumptions how to optimize the process. First, it is necessary to take into account the nucleophilic reactivity of HCl and HP. If their concentrations will be comparable, there will be virtually no competition for the carbocation because of high nucleophilicity of HP. Therefore, it seems necessary and justified to ensure excess of HCl by rapid saturation of the reaction mixture with it. Second, to reduce the HP concentration, it is necessary to ensure conditions for shifting the equilibrium toward OP formation. For this purpose, the aldehyde should also be taken in excess. The reagents are taken in excess also because of the fact that the certain fraction of the aldehyde and HCl inevitably passes into the aqueous layer forming a separate phase with the progress of the reaction.

Thus, to increase the yield and selectivity with respect to CP, it is necessary to take the aldehyde and HCl in excess relative to HP. However, this apparent advantage in the step of the CP synthesis transforms into a serious disadvantage in the step of target product isolation from the reaction mixture. Therefore, the excess of these reagents should be minimum necessary. To find the optimum reactant ratio in reaction (2), we performed a special study and determined the optimum HP : aldehyde : HCl molar ratio to be 1 : (1.01–1.05) : (1.05–1.30), respectively. The use of the reactants in this ratio allows CP to be obtained in a yield as high as 97% based on HP, with no DP by-product found in the reaction mixture.

The experimental substantiation of the above reactant ratio was proved by experiments on studying the effect of the excess of acetaldehyde and HCl on the yield of α-chloroethyl *tert*-butyl peroxide (**I**). The yield of **I** was estimated from the residual content of available oxygen, AO, in the reaction mixture after its decomposition with triethylamine under the conditions recommended in [16]. We found that the yield of **I** was virtually independent of the excess of acetaldehyde and reached 95 and 97% with the 5 and 20% molar excess, respectively, although the accumulation of **I** at 20% excess occurred faster.

The curves of HCl accumulation in the reaction mixture, obtained by titration of hydrolyzable chlorine with a 0.5 N alcoholic KOH solution, are shown in

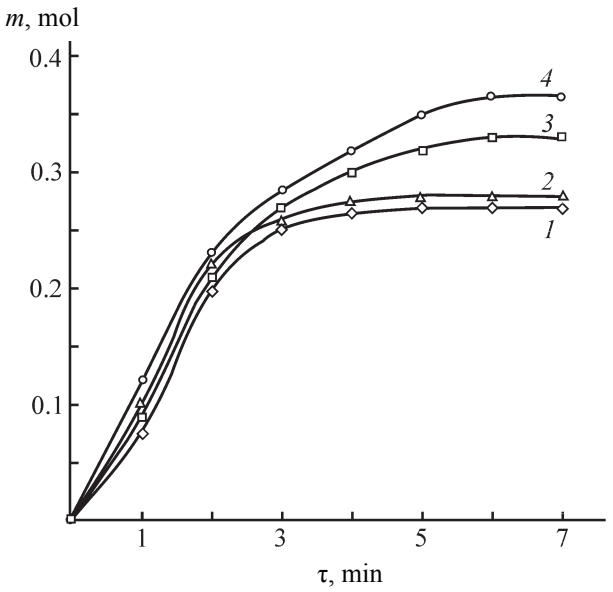


Fig. 1. Effect of excess acetaldehyde on the accumulation *m* of (*1, 2*) **I** and (*3, 4*) HCl in the reaction mixture. (τ) Time; the same for Fig. 2. Molar excess of acetaldehyde, %: (*1, 3*) 5 and (*2, 4*) 20.

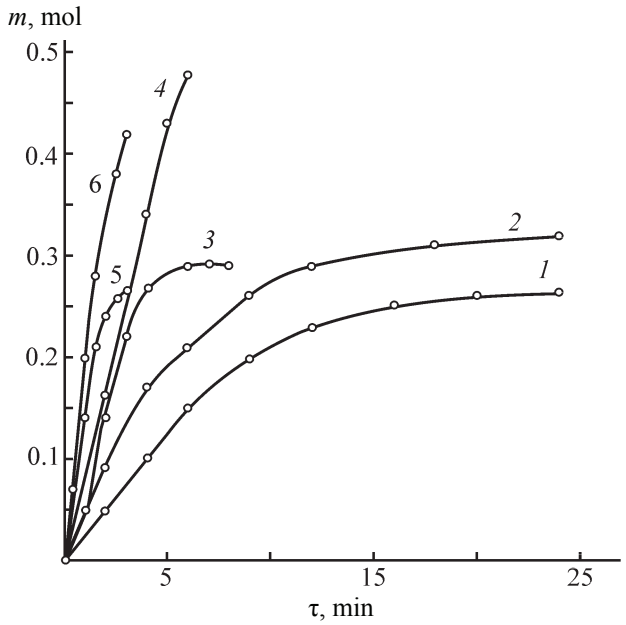


Fig. 2. Influence of the HCl feeding rate on the accumulation m of (*2, 4, 6*) HCl and (*1, 3, 5*) I in the reaction mixture. Feeding rate, mL min^{-1}: (*1, 2*) 0.3, (*3, 4*) 2.9, and (*5, 6*) 5.2.

Fig. 1. As can be seen, the reaction of HCl with the intermediate OP starts without induction period, which confirms the carbocation formation in reaction (2). Also, it can be noted that the HCl concentration in the reaction mixture is higher than the concentration of **I** and that this difference increases with time as the reaction products are accumulated.

The influence of the HCl feeding rate on the yield of **I** was studied at the initial amounts (mole) of HP and acetaldehyde of 0.3 and 0.315, respectively (Fig. 2). As seen from Fig. 2, initially the rate of accumulation of **I** is essentially the same as the rate of feeding HCl, but at deeper conversion the accumulation of **I** in the reaction mixture noticeably decelerates. At lower rate of feeding HCl, the deceleration is observed earlier. For example, in the curves of accumulation of **I** at HCl feeding rates of 0.3 and 2.9 mL min^{-1}, the deceleration is apparent and corresponds to 60 and 95% yield of **I**, i.e., the formation of **I** directly depends on the rate of feeding HCl. The highest yield of **I** (97%) is observed when HCl is fed at a rate of 2.9 mL min^{-1}.

Isolation of CPs from the reaction mixture is a separate problem. First, these compounds are thermally unstable; second, the reagents present in excess are capable not only to catalyze the CP decomposition, but also to react with agents used in further work-up. The classical approach to solution of this problem is vacuum distillation of the reaction mixture with the preliminary removal of the solvent. However, vacuum distillation is insufficiently efficient because of inevitable losses and is practically unfeasible because of thermal instability of CPs. Therefore, we chose another approach consisting in stabilization of CP by binding excess HCl. The choice of stabilizers for CP is restricted by its high reactivity. Amines, alkali and alkaline-earth metal hydroxides, and alkali metal carbonates and hydrocarbonates are unsuitable for this purpose, because they react with CP with the cleavage of the O–O bond [15]. Urea and calcium carbonate, which do not react with CP, were suggested as stabilizers. As we found, unstabilized solutions of **I** can be stored at 8–10°C for no more than 1 h, after which the compound starts to decompose via cleavage of the O–O bond (Table 1), and in 5 h the compound completely decomposes with tarring of the reaction mixture. Storage of solutions of **I** after preliminary treatment with urea or calcium carbonate does not lead to noticeable decomposition of CP, even after storage for 24 h at room temperature. The AO content in a chloroform solution of **I** was determined by the procedure described in [16].

After treatment of the reaction mixture with urea or calcium carbonate, taken in a molar ratio of (0.05–0.1) : 1 to CP, it is unnecessary to isolate CP by distillation, and the stabilized solution can be used for the synthesis of, e.g., OP ethers [6, 9, 10, 17] and esters. Calcium carbonate

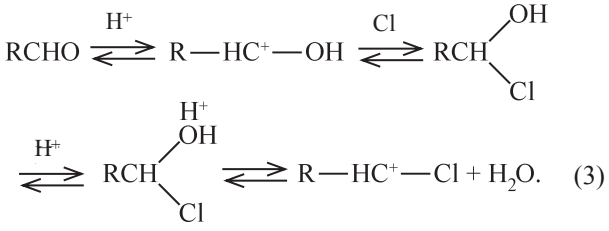
is preferable as stabilizer, because it does not require preliminary treatment before use and, in contrast to urea, is nonhygroscopic, which is particularly important, because CPs are readily hydrolyzed in the presence of moisture, i.e., treatment of CP solutions with urea or calcium carbonate allows their reliable storage for 24 h.

The temperature at which the CP synthesis is performed is mainly determined by the stability of the C–Cl bond, which, in turn, is determined by the structure of the radical in the α-position to the O–O bond, i.e., by the structure of the starting aldehyde. For aliphatic aldehydes, the synthesis temperature should not exceed 5–10°C.

Thus, to prepare CP, it is necessary to take the aldehyde and HCl in no less than 5% and no more than 20% molar excess, respectively, relative to HP. Isolation of the target products should be performed after treatment of the reaction mixture with urea or calcium carbonate, followed by solvent removal if necessary.

Thus, synthesis of CPs using aliphatic aldehydes consists of five main steps: (1) cooling of an aldehyde solution in chloroform to ~10°C, (2) addition of HP to the aldehyde solution at a temperature no higher than 10°C, (3) cooling of the reaction mixture to –10°C, (4) feeding of HCl to the reaction mixture at a temperature no higher than 5°C, and (5) isolation of the target product.

Synthesis of CPs via geminal chlorohydrins. Geminal chlorohydrins are intermediates in reactions of nucleophilic addition of Cl^- to carbonyl compounds under the conditions of acid catalysis and practically are not used as reagents for organic synthesis because of their extremely low stability:



(3)

Reaction (3) starts with addition of proton to the C=O bond and yields a carbocation RHC^+–OH, which is attacked by the Cl^- ion to form a chlorohydrin and then a carbocation RHC^+–Cl. Analyzing reaction (3), we can conclude that a series of equilibrium processes in reaction of an aldehyde with HCl inevitably results in formation of two carbocations, with each of them present in an equilibrium concentration. It is natural to assume that introduction of stronger nucleophiles into this system will favor their efficient interaction with intermediate carbocations. This assumption is confirmed in an experiment on using HP as reagent in reaction (4), with no less than 94% yield of the corresponding CPs (Table 2):

Table 1. Stabilization of chloroform solutions of **I**

Storage time, h	AO content of **I**, %		
	stabilized solution of **I** at 20°C		unstabilized solution of **I** at 8–10°C
	with urea	with calcium carbonate	
0	6.45	6.50	6.70
1	6.30	6.45	6.12
2	6.26	6.40	4.25
5	6.18	6.42	Vigorous evolution of HCl, tarring
24	6.06	6.30	

$$(CH_3)_3COOH + [RC^+HCl] \longrightarrow [(CH_3)_3COOC^+H(R)Cl] \longrightarrow (CH_3)_3COOCH(R)Cl + H^+. \quad (4)$$

Because the solubility of HCl in the reaction mixture is limited, initially it can be introduced in an amount of ≤30 wt % relative to the required amount. Further feeding of HCl leads to its breakthrough and nonproductive consumption. Therefore, the addition of HP should be started only after introducing 30 wt % of HCl, with simultaneous feeding of the remaining amount of HCl. By so doing, it becomes possible, first, to increase the HCl solubility in the reaction mixture, second, to shift the equilibrium of reaction (3) toward formation of chlorohydrin, and, third, to efficiently utilize the starting reactants.

Table 2. Physicochemical characteristics and yields of $(CH_3)_3COOCHRCl$

R	Yield, %	T_b, °C (3 mmHg)	n_D^{20}	d_4^{20}	AO, %	
					found	calcd.
Me(I)	97.0	25–26	1.4202	0.9241	9.95	10.05
Et	94.5	34–36	1.4221	0.9720	9.60	9.65
i-Pr	94.0	42–43	1.4293	0.9660	8.82	8.90
Pr	95.4	45–46	1.4224	0.9656	8.84	8.90

After adding HP, one can expect parallel occurrence of several reactions, because formally the reaction mixture contains aldehyde, HCl, and carbocations. However, this is not the case. If HP reaction (1) between HP and the aldehyde took place, under the conditions of reaction (4) the major product would be DP, but actually it is not formed in noticeable amounts. Apparently, CP is mainly formed by reaction (4), but also the parallel reaction of HP with the carbocation RHC^+–OH [reaction (3)] cannot be ruled out. This reaction yields OP, which undergoes hydrochlorination under the conditions of reaction (4) to form CP by reaction (2). Because both pathways yield the same target product, it makes no sense to estimate the contribution of the reaction of HP with the carbocation RHC^+–OH.

It follows from the above analysis that HP does not react with the aldehyde under these conditions, because by the moment of HP appearance the effective concentration of the reactive carbocations RHC^+–Cl is already present in the reaction mixture. It is quite obvious that the HP as a "supernucleophile" will primarily react specifically with this carbocation and shift the equilibrium in reaction (3) toward CP formation.

Thus, we have shown for the first time that the reaction of geminal chlorohydrins with HP can yield CP and can be performed in four steps instead of five, with the second and third steps practically coinciding in time: (1) cooling of an aldehyde solution in chloroform to 5°C, (2) feeding of 30 wt % of HCl into the aldehyde solution at a temperature no higher than 10°C, (3) gradual feeding of HP and the remaining HCl at a temperature no higher than 15°C, and (4) isolation of the target product.

In CP synthesis by reaction (4), the process monitoring is simplified. The maximal heat release is observed in the second step, when the reaction mixture contains no peroxy compounds and, therefore, there are no problems with their possible decomposition. When performing synthesis by reaction (1), the reaction of HP with an aldehyde in the second step is accompanied by strong heat release (142.7 kJ mol^{-1}) and requires additional cooling to avoid acid-catalytic and thermal decomposition of peroxides. Therefore, it becomes possible in the third step to increase the temperature to 15°C and to perform the process more intensely than via reaction (1).

In CP synthesis via chlorohydrin, it becomes unnecessary to use excess aldehyde, but excess HCl is necessary for shifting the equilibrium in reaction (3) toward formation of the RHC^+–Cl carbocation. The aldehyde : HCl : HP molar ratio should be 1 : (1.2–1.3) : 1, respectively.

CP analysis. From the technological viewpoint, it is more appropriate to use a CP without its isolation from the reaction mixture. For this purpose, we developed an analytical method for the determination of CP concentration in a mixture with other peroxides, which would allow more efficient use of CP and other reagents for preparing functional dialkyl peroxides and quantitative estimation of the DP impurity in CP transformation products [16].

CPs are more reactive than DPs, primarily because of the presence of the C–Cl bond. For example, CPs are readily hydrolyzed with water with the release of HCl whose content can be determined by classical methods. However, it is impossible to calculate the CP concentration from the HCl content, because the reaction mixture always contains a certain excess of HCl. Therefore, the choice of conditions for separate determination of the concentrations of CP and DP in their mixture is based on the reaction of CP with TEA, involving all the three reaction sites (O–O, C–H, C–Cl) of CP [15, 18]. TEA reacts with CP with the cleavage of the O–O bond, leaving the O–O bond in DP intact. The reaction starts with the formation of a complex of CP with TEA via C–Cl bond:

$$(CH_3)_3COOCH(R)Cl + N\equiv \longrightarrow [(CH_3)_3COOCH(R)N\equiv]^+Cl^-, \quad (5)$$

After that, the amine hydrochloride is eliminated with the cleavage of the C–H bond:

$$[(CH_3)_3COOCH(R)N\equiv]^+Cl^- \longrightarrow \equiv N\cdot HCl + [(CH_3)_3COO(R)C\colon].$$

The *tert*-butylperoxycarbene arising in the process is unstable and transforms into nonperoxy compounds via cleavage of the O–O bond:

$$[(CH_3)_3COO(R)C\colon] \longrightarrow \begin{cases} (CH_3)_3COC(O)R, \\ (CH_3)_3COH + MHBC. \end{cases} \quad (6)$$

where MHBC is a mixture of high-boiling components.

The iodometric analysis of the DP (prepared by the method of [19]), performed before and after its treatment with TEA for 1 h, showed that the AO concentration did

not change noticeably, e.g., DP did not decompose in the course of the analysis. Thus, after the treatment of a mixture of peroxides with TEA, only one peroxide, DP, remains in the reaction mixture, so its concentration can be determined by iodometric titration, and the CP concentration can be calculated as the difference between the total content of peroxides in the mixture and the DP content.

It should be noted that TEA should be dried for the use in the analysis, because the CP hydrolysis is accompanied by the release of HP [15], which is decomposed by TEA more slowly, distorting the analysis results. The weight ratio of TEA and the mixture being analyzed should be 0.7 : 1.0, respectively. DP is a difficultly reducible peroxy compound; therefore, the procedure for quantitative determination of AO in it involves more severe conditions than in the analysis of OP or CP. As found in [20], peroxy acetals are quantitatively reduced in 15 min at 70°C in the presence of hydroiodic acid generated in situ by the reaction of KI with a 40% HBr solution.

The decomposition time for **I** is 25 min at 25°C; in chloroform solution, which is used most frequently in the CP synthesis, it completely decomposes in 20 min. In hexane, this reaction occurs in 2 h. Therefore, when CPs are analyzed in hydrocarbon solvents, the solutions should be diluted with an equal amount of chloroform prior to adding TEA.

Thus, the method developed allows sufficiently accurate determination of the CP and DP concentrations in their mixture. This method allows monitoring of the CP concentration, opening the possibility of using CPs as starting compounds for preparing functional dialkyl peroxides without preliminary isolation of CPs from the reaction mixture and of appreciably simplifying the CP work-up technology by reducing the number of process steps.

SYNTHESIS OF OP ESTERS AND ETHERS

Synthesis of OP esters. OP esters are prepared by OP acylation with acid anhydrides or chlorides [13] or by alkylation of carboxylic acid salts with CPs. The latter procedure is the most promising, because it allows CPs to be used without their isolation from the reaction mixture:

$$R'C(O)OM + ClCH(R)OOC(CH_3)_3 \longrightarrow R'C(O)OCH(R)OOC(CH_3)_3 + MCl,$$

where R = CH_3, H; R' = CH_3, C_2H_5, C_3H_7, C_7H_{15}–C_9H_{19}, C_6H_5, CF_3, $CF_3(CF_2)_n$; M = K, Na.

The reaction of CPs with sodium or potassium salts of carboxylic acids, which are insoluble in organic solvents, occurs at the interface at 40–50°C for 1.5–3.0 h with the target product yield of 41–60%. Apparently, to accelerate the process, it should be performed under homogeneous conditions. To this end, we searched for an acylating agent soluble in organic solvents. It could be expected that triethylammonium complexes of carboxylic acids would be such agents. However, actually acylation with triethylammonium complexes occurred unselectively and was accompanied by the cleavage of the O–O bond in the CP. Iodometric analysis showed that the total content of AO in the reaction mixture by the end of the synthesis decreased by 35–40% relative to the initial content. For example, α-pelargonyloxyethyl *tert*-butyl peroxide (II) was obtained in 60% yield. The following by-products were detected in the reaction products by gas–liquid chromatography (mole per mole of **I**): *tert*-butyl acetate (0.23), TB (0.11), pelargonic acid (0.35), and TEA hydrochloride (0.78). The formation of *tert*-butyl acetate and TB and a decrease in AO in the reaction mixture indicate that compound **I** decomposes under the action of TEA via intermediate carbene formation by reactions (5) and (6). The lack of balance with respect to TEA hydrochloride suggests that, along with the above-indicated decomposition pathway of **I**, there also can be another pathway yielding unstable dimethylvinylamine whose existence was proved by spectroscopy in [21]. Thus, the results of the experiment suggest the presence of free TEA in its equimolar mixtures with monocarboxylic acids. To prove this hypothesis, we mixed equimolar amounts of acetic acid (AA, pK_a 4.75) and TEA, after which we added an equimolar amount of the weaker pelargonic acid (pK_a 4.90) and acylated **I** with the resulting mixture. The reaction products contained α-acetyloxyethyl *tert*-butyl peroxide **III** and compound **II** in a molar ratio of 1 : 0.36 (R_f 0.6 and 0.75, respectively). The AO content in the mixture decreased by 23%. Similar result was obtained when adding AA under the same conditions. When AA was taken in a twofold excess relative to TEA, the yield of **III** increased by 15% (Table 3). When the acylation was performed in AA medium (AA–TEA ratio 57 : 1), the AO content in the reaction mixture after the end of the reaction did not change noticeably. Thus, complete binding of TEA is possible only in the presence of a large excess of the acid.

Table 3. Effect of solvent and AA : TEA ratio on the time of acylation of **I** and on the yield of **III** at 20°C

Solvent	ε_{25}	P_j	E_j	AA : TEA ratio	Time, min	Yield, %
Hexane	1.9		0	1 : 1	300	63.0
				2 : 1	60	72.0
Chloroform	4.7	0.35		1 : 1	4	60.0
				2 : 1	4	75.0
Water	78.5	0.55		1 : 1	4	35.0
TB	12.2	0.58		1 : 1	4	41.0
				2 : 1	5	70.0
AA	6.2	1.2		57 : 1	3	85.0
Acetone	20.0		0.93	1 : 1	90	62.0
				2 : 1	60	75.0
DMF	36.7		1.17	1 : 1	5	80.0

However, product **III** was isolated in only 85% yield, which may be due to its loss in the course of isolation from the acetic acid solution. The experimental data obtained are given in Table 3. As solvent characteristics we used the acidity factor P (reference phenol, $P_i = 1$) or basicity factor E (standard diethyl ether, $E_j = 1$) [22].

It is known [23, 24] that the capability of acid molecules for self-association leads to the formation, along with the complexes $RCOOH{\cdot}NR_3$, of more stable higher complexes $(RCOOH)_n{\cdot}NR_3$. Therefore, a certain amount of the amine remains unbound in equimolar mixtures of a carboxylic acid with TEA, which leads to the side reaction of CP decomposition and to a decrease in the yield of the target product.

The experimental data (Table 3) demonstrate a considerable effect of solvents on the time and selectivity of the acylation. For example, in hexane the reaction takes 5 h, whereas in polar solvents it is complete in 4 min. This large difference in the reaction times is probably determined by the reactivity of both reactants.

The formation of the structure of the complex is determined by a number of factors, primarily by the proton-donor properties of the acids, proton-acceptor properties of the amines, and solvating power of the solvent. By varying these properties, it is possible to control reaction (7):

$$AH + NR_3 \rightleftharpoons AH\cdots NR_3 \rightleftharpoons A\cdots HN^+R_3 \rightleftharpoons A\cdots SH\cdots NR_3 \rightleftharpoons A + HN^+R_3. \quad (7)$$

From the viewpoint of acylation, the conditions favoring the formation of ionic complexes, up to free ions, are the most favorable.

The equilibrium in reaction (7) largely depends on the solvent [22]. In proton-donor solvents, the equilibrium is shifted toward the ion pair owing to hydrogen bonding of the solvent (S–H) with the carbonyl group of the molecular complex. Therefore, the acylation of CP with the ionic complex occurs within 3–5 min. The yields of product **III** in different proton-donor media are essentially different. For example, in water the process is complicated by the hydrolysis of CP; therefore, the yield does not exceed 35%. In TB, the yield of **III** was also low. However, TB does not react with **I**, which is confirmed by the absence of reaction products different from those obtained by the acylation in chloroform. This is apparently due to the competition of TB with AA for TEA, which probably leads to the formation of species of more complex composition than in chloroform. An increase in the yield of **III** in TB to 70% suggests that the twofold excess of AA virtually suppresses the competition of TB for TEA, and the amount of the free amine decreases.

In inert solvents, the equilibrium in reaction (7) is shifted toward formation of molecular complexes; therefore, the acylation of **I** in hexane occurs within 5 h. However, the use of a twofold excess of AA allows the reaction time to be decreased by a factor of 5. This is apparently due to the shift of the equilibrium in reaction (7) toward formation of the ionic complex, so that the yield of **III** increases.

The acylation time of **I** in proton-acceptor solvents is different. For example, in DMF the process is complete in 5 min, whereas in acetone it lasts for 1.5 h. Similarly to the reaction in hexane, with a twofold excess of AA in acetone the reaction occurs faster (in 1 h). The highest yield of **III** was obtained in DMF, because this solvent creates the most favorable conditions for the formation of the complexes $CH_3COOH{\cdot}N(C_2H_5)_3$ and for a decrease in the content of bound TEA in the reaction mixture.

The polarity of the medium favors ionization not only of the acylating complex [reaction (7)], but also of CP [reaction (8)], which is solvated with chloroform by hydrogen bonding with the leaving group:

Table 4. Physicochemical characteristics and yields of OP esters $(CH_3)_3COOCH(CH_3)OC(O)R$

R	R_f [a]	MM		AO, %		n_D^{20}	d_4^{20}	Yield, %
		found	calculated	found	calculated			
CH_3	0.60	174	176	8.76	9.09	0.9402	1.4080	95
$C(CH_3)_3$	0.74	215	218	7.53	7.34	0.9125	1.4109	95
$CH(CH_3)_3$	0.64	202	204	7.88	7.84	0.9920	1.4090	94
$(CH_2)_2CH_3$	0.62	200	204	7.80	7.84	0.9324	1.4115	95
$(CH_2)_4CH_3$	0.67	227	232	6.89	6.89	0.9386	1.4200	95
$(CH_2)_7CH_3$	0.75	268	274	5.80	5.83	0.9050	1.4250	92
$C_{17}H_{35}$	0.70	402	400	3.90	4.00	0.8991	1.4395	85
$C_{17}H_{33}$	0.71	374	398	3.95	4.02	0.9007	1.4490	85
C_6H_5	0.60	224	238	6.60	6.72	1.0402	1.4783	90
$C_{10}H_{15}$ (adamantly)	0.69	293	296	5.40	5.41	1.0252	1.4760	86

[a] Silufol UV-254, eluent hexane–diethyl ether (15 : 5 by volume), visualization with iodine vapor.

$$(CH_3)_3COOCH(R)Cl\cdots HCCl_3 \rightleftharpoons [(CH_3)_3COOC^+HR\cdots Cl^-\cdots HCCl_3]. \quad (8)$$

In the process, the negative charge is concentrated on the leaving group, and the strength of such hydrogen bonds in the activated state is considerably higher than in the initial state. Such specific solvation leads to additional stabilization of the activated state of CP in proton-containing media, increasing the degree of its ionization and decreasing the acylation time. In chloroform, AA–pyridine complexes exist in the molecular form [22] but acylate CP within 5 min; therefore, it can be stated that the acylation time is mainly determined by the extent of CP ionization, rather than by the structure (molecular or ionic) of the acylating complex.

A study of the regular trends in CP acylation with carboxylic acid–TEA complexes has shown that the composition of the acylating complex determines mainly the reaction selectivity, whereas the solvent polarity determines the acylation time.

The optimum conditions are those under which 1 : 1 complexes are formed. The conditions reducing the self-association of acids and hence favoring the formation of the complexes $RCOOH\cdot NR_3$ are dilution and excess amine [25]. The use of 9×10^{-3} M solutions of AA in chloroform for preparing the acylating complex leads to the preparation of **III** in 80% yield, i.e., the side reaction of CP decomposition under the action of unbound TEA is not fully excluded in this case. Hence, none of the two approaches can ensure successful acylation of CP.

In our studies we found the conditions for the formation of the 1 : 1 complex owing to the artificially created excess of the amine by dosing the acid into a chloroform solution of TEA (1 M) in the adiabatic mode at such a rate that the temperature of the reaction mixture changed by no more than 5°C. Under these conditions, the yields of OP esters in chloroform increased to 95% (Table 4). Thus, we suggested for the first time the use of a new acylating agent in the form of a complex of a carboxylic acid with a tertiary amine, with chloroform as a solvent. We were able to perform the CP acylation within 4 min under adiabatic conditions at equimolar ratio of the reactants.

Thus, we found that the CP acylation should be performed at an equimolar ratio of CP and acylating complex in a chloroform solution, that the acylating complex should be prepared under adiabatic conditions by dosing the acid to TEA in a molar ratio of 1 : 1 in chloroform, and that the reaction progress should be monitored by variation of pH of the reaction mixture (the reaction is considered to be complete at pH 6.0–7.0).

The synthesized OP esters are colorless liquids with ester odor, readily soluble in organic solvents and insoluble in water. They do not change their properties after 1-year storage. The structure of the synthesized peroxides was proved by the analysis for AO and by

Table 5. Physicochemical characteristics and yields of OP ethers $(CH_3)_3COOCH(CH_3)OR$

R	T_b, °C (P, mmHg)	MM		AO, %		n_D^{20}	d_4^{20}	Yield, %
		found	calculated	found	calculated			
$CH_2CH(CH_3)_2$	30 (1)	180	190	8.45	8.42	0.9125	1.4078	94
C_6H_{11}-*cyclo*	60 (1)	210	216	7.50	7.41	0.9199	1.4370	94
$(CH_2)_2CH_3$	–	178	176	8.98	9.09	0.8748	1.4060	95
CH_3	31 (13)	150	148	8.84	9.09	0.8782	1.4085	90

molecular mass determination and was confirmed by the IR and ^{1}H NMR spectra. The IR spectra contain a strong band at 1720–1740 cm^{-1}, characteristic of C=O stretching vibrations, and a band at 860–880 cm^{-1}, characteristic of O–O stretching vibrations. In the ^{1}H NMR spectra, there are the following characteristic signals (δ, ppm): 1.22 s [9H, $(CH_3)_3C$], 4.65 q, J 5.4 Hz (1H, O–O–CH), 1.22 d, J 11.7 Hz (3H, O–O–CH–CH_3); these signals are present in the spectra of all the molecules. The ^{1}H NMR spectra of the synthesized OP esters differ in the proton signals of the radical in the acyl moiety.

The new acylating agent, a 1 : 1 complex of a carboxylic acid with a tertiary amine, is effective in reactions not only with CPs, but also with chloro ethers, benzyl chloride, allyl chloride, and alkyl halides in which the chlorine atom is bound to a tertiary carbon atom.

Synthesis of OP ethers. Alcoholysis of CPs occurs at 30–70°C within 2.5–6.0 h in an inert solvent with continuous removal of HCl with a stream of dry nitrogen. The yield of the target peroxides is 53–75% [6, 9]:

$$ROOCH(R')Cl + HOR'' \longrightarrow ROOCH(R')OR'' + HCl,$$

R = CH_3, $C(CH_3)_3$; R' = H, CH_3, C_2H_5; R'' = $CH_2CH_2CH_3$, $CH_2CH(CH_3)_2$, *cyclo*-C_6H_{11}, $CH_2CH(NO_2)CH_3$, $CH_2(CH_2OCH_2)_2CH_2OH$, $CH_2CH(OH)CH_2OH$, –[CH_2–CH–]$_n$–.

Relatively low yields of OP ethers are due to the presence of HCl in the reaction mixture, because HCl, being partially soluble in chloroform, is removed with an inert gas stream incompletely, and also to elevated temperature and long time of the reaction, favoring catalytic decomposition of the starting CP. Therefore, as acceptor of the released HCl we took calcium carbonate used for stabilization of chloroform solutions of CPs. With calcium carbonate, we were able to perform the CP alkylation at 20–30°C within 10–30 min, to increase the yield of the peroxides to 95% (Table 5), and to simplify the isolation of OP ethers by eliminating the step of reaction mixture neutralization and reducing the amount of wastewater. The starting alcohols, compound **I**, and calcium carbonate were taken in a molar ratio of 1 : 1 : (0.51–0.58), respectively [10, 17]. The physicochemical characteristics of the synthesized OP ethers are in agreement with the published data.

Using various hydroperoxides as nucleophiles instead of alcohols, we obtained symmetrical and unsymmetrical diperoxides.

EXPERIMENTAL

The IR absorption spectra of OP ethers and esters were recorded in the range 500–4000 cm^{-1} with a Specord UV-VIS spectrophotometer from thin films, and the ^{1}H NMR spectra, with a Varian Mercury Plus-300 spectrometer operating at 300 MHz, with HMDS as internal reference. The content of AO in CPs was determined by the standard procedure, and that in ethers and esters, by the procedure described in [20]. Carboxylic acids, alcohols, and chloroform were purified and dried by the standard procedures [26].

Synthesis of I and III. A reactor equipped with a thermometer and a gas-feeding tube with a porous plate was charged with 9.2 g (0.21 mol) of acetaldehyde in 50 mL of chloroform, after which 18 g (0.2 mol) of HP was added at a temperature not exceeding 10°C. The reaction mixture was cooled to –10°C, and a flow of 8.0 g (0.22 mol) of dry HCl was passed. In the process, the temperature no higher than 5°C was maintained. The organic payer was separated from the aqueous layer and treated with 1 g (0.01 mol) of calcium carbonate.

The resulting chloroform solution of **I** was filtered and mixed with 32.2 g (0.2 mol) of the complex of

triethylamine with acetic acid in 100 mL of chloroform. After the lapse of 5 min, the reaction mixture was washed with water, a 2% KOH solution, and again with water. After removing the solvent, 32.9 g (92%) of the product was obtained, n_D^{20} 1.4078, AO 8.79%.

Synthesis of α-chloropropyl *tert*-butyl peroxide and α-acetyloxypropyl *tert*-butyl peroxide. A reactor equipped with a dropping funnel, a thermometer, and a gas-feeding tube with a porous plate was charged with 11.62 g (0.2 mol) of propionaldehyde in 50 mL of chloroform. The solution was cooled to 10°C, and 2.6 g of dry HCl was passed. After that, at a temperature no higher than 10°C, 18 g (0.2 mol) of HP was added dropwise, with simultaneous feeding of the residual amount (6.2 g) of dry HCl in the course of 18–20 min. The total amount of dry HCl was 8.3 g (0.24 mol). After that, the organic layer was separated, dried over calcium chloride, and analyzed for the CP content. Yield 31.6 g (95% based on HP). The chloroform solution of CP was filtered and then mixed with 32.2 g (0.2 mol) of the complex of triethylamine with acetic acid, dissolved in 100 mL of chloroform, at 30°C. After the lapse of 5 min, the reaction mixture was washed with water. The solvent was removed, and α-acetyloxypropyl tert-butyl peroxide was obtained; yield 32 g (91% based on HP), n_D^{20} 1.4120, AO 8.39%.

Synthesis of I. The compound was prepared similarly from 8.8 g (0.2 mol) of acetaldehyde. Yield of **I**, according to analysis results, 29.3 g (96% based on HP). The solvent was distilled off, and the reaction mixture was distilled with the collection of the fraction boiling at 40–42°C (12 mmHg). Yield of **I** 24.4 g (80%), n_D^{20} 1.4190, AO 10.05%.

Synthesis of α-butoxyethyl *tert*-butyl peroxide. A reactor equipped with a stirrer, a thermometer, and a dropping funnel was charged with 4.32 g (0.0432 mol) of calcium carbonate, a solution of 5.9 g (0.08 mol) of butanol in 12 mL of chloroform was added, and a solution of 12.2 g (0.08 mol) of **I** in 25 mL of chloroform was added from the dropping funnel with stirring. The mixture was stirred at 20–30°C for 30 min until pH 7.0 was attained, after which the calcium chloride precipitate was filtered off, the filtrate was washed with water and dried over calcined magnesium sulfate, the chloroform was distilled off in a water-jet-pump vacuum, and the residual solvent was removed by evacuation at 30–40°C/100 mmHg. Yield of α-butoxyethyl *tert*-butyl peroxide 14.4 g (95%), n_D^{20} 1.4056, d_4^{20} 0.9174, AO 8.50%.

CONCLUSIONS

(1) The reaction of hydroperoxides with aldehydes and hydrogen chloride as a route to α-chloroalkyl peroxides was studied. Conditions were found for preparing α-chloroalkyl peroxides via chlorohydrin; this intermediate can be used without isolation from the reaction mixture.

(2) A new procedure was developed for preparing α-hydroxyalkyl peroxide esters from chloroalkyl peroxides using a new acylating agent, a complex of a carboxylic acid with triethylamine. Conditions were found for the formation of the 1 : 1 complex. The acylation selectivity in solvents of different polarity is determined by the composition of the complex, and the reaction time, by the extent of ionization of α-chloroalkyl peroxides.

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