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Interaction of 9-Substituted Anthracenes with Oxidation Systems *tert*-Butylhydroperoxide–Metal *tert*-Butoxide

L. P. Stepovik[a], **Yu. B. Malysheva**[a], **and G. K. Fukin**[a,b]

[a] *Lobachevsky State University of Nizhny Novgorod, pr. Gagarina 23, Nizhny Novgorod, 603950 Russia*
e-mail: lstepovik@mail.ru

[b] *Razuvaev Institute of Organometallic Chemistry of Russian Academy of Sciences, Nizhny Novgorod, Russia*

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Abstract—9-R-Anthracenes (R = Me, Ph) are effective acceptors of peroxyl and metalalkoxyl radicals in the systems *tert*-butylhydroperoxide–metal *tert*-butoxide (M = Al, V, Cr; C_6H_6, 20°C). Isolation of 9-R-9,10-dihydro-9,10-di-*tert*-butylperoxyanthracenes, 10-R-10-*tert*-butylperoxy-9-anthrones as major products reliably confirms the formation of *tert*-butylperoxy radicals and can be used for quantitative assessment of their content.

Keywords: 9-alkyl(aryl)anthracenes, *tert*-butylhydroperoxide, metal *tert*-butoxides, peroxyradicals, oxidation, 9-alkyl(aryl)peroxyanthracenes, X-ray

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Interaction of *tert*-butylhydroperoxide **I** with *tert*-butoxides of aluminum, titanium, zirconium, vanadium, chromium includes the stages of formation of metal-containing peroxides and trioxides [1–6]. The main product of decomposition of the latters is oxygen, partly in the singlet state. Simultaneously, the homolysis of peroxide bonds occurs [scheme (1)].

The direction of decomposition of trioxides depends both on the metal and the ratio of the starting components. The yield of singlet oxygen was determined from the products of its reaction with anthracene and 9,10-dimethylanthracene. All oxygen-containing radicals were identified by ESR method in the form of their spin-adducts with nitrones.

Chemical identification of alkylperoxyl radicals is of interest both from the viewpoint of their quantitative assessment and investigation of the reaction mechanisms and of the synthesis of new unsymmetrical peroxides. Derivatives of this type were obtained in the reactions of radicals $ROO^{\bullet}$ with some aromatic amines [7] and sterically hindered phenols [2, 8–10]. The reaction of hydroperoxide **I** with 9,10-dimethylanthracene in the presence of alkoxy-derivatives of transition metals (acetylacetonates of cobalt, chromium, vanadium, tetra-*tert*-butoxychromium) is described [6, 11]. As the main products, 9,10-dimethyl-9,10-dihydro-9,10-di-*tert*-butylperoxyanthracene, 10-methyl-10-*tert*-butylperoxy-9-anthrone and 9,10-dimethyl-9,10-epidioxyanthracene were isolated.

In the present study the reaction of 9-methylanthracene (9-MA) and 9-phenylanthracene (9-PA) with hydroperoxide **I** was studied in the presence of *tert*-butoxides of aluminum $Al(OBu\text{-}t)_3$, vanadium $V(OBu\text{-}t)_4$, chromium $Cr(OBu\text{-}t)_4$ in order to further investigate the oxidative potential of the system *t*-BuOOH–metal alkoxide, to identify the intermediates and final products.

All reactions were performed in the solvent which is non-oxidizable by the studied systems, benzene, at 20°C and the molar ratio 9-R-anthracene–**I**–metal alkoxide equal to 1 : 5 : 1. The reaction mixtures were kept for 2 days at 20°C, but the reaction products **II**–**VIII** were detected already after 3 h. As was preliminarily shown, alkylanthracenes do not react

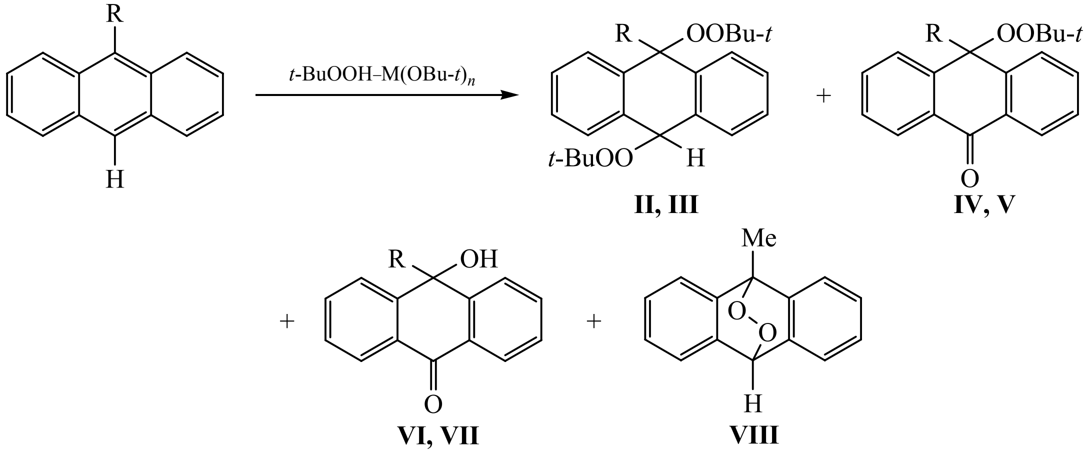
$$[M]OBu\text{-}t \xrightarrow[t\text{-BuOH}]{t\text{-BuOOH}} [M]OOBu\text{-}t \xrightarrow[t\text{-BuOH}]{t\text{-BuOOH}} [M]OOOBu\text{-}t \begin{cases} \xrightarrow{a} {}^1O_2,\ {}^3O_2 + [M]OBu\text{-}t, \\ \xrightarrow{b} [M]\dot{O} + \dot{O}OBu\text{-}t + [M]O\dot{O} + \dot{O}Bu\text{-}t. \end{cases} \tag{1}$$

Table 1. Products of reaction of 9-R-anthracenes with *t*-BuOOH in the presence of Al, V, Cr *tert*-butoxides (molar ratio 1 : 5 : 1, C_6H_6, 20°C, in moles per 1 mol of the substrate)

Reaction products[a]	$Al(OBu\text{-}t)_3$		$V(OBu\text{-}t)_4$		$Cr(OBu\text{-}t)_4$	
	R = Me	R = Ph	R = Me	R = Ph	R = Me	R = Ph
O_2	0.97	1.42	–	–	0.19	0.20
Me_2CO	Traces	Traces	0.02	0.03	0.04	0.07
t-BuOH	5.64	5.44	3.76	3.53	6.19	6.58
$(t\text{-}BuO)_2$	0.02	0.02	0.03	0.05	0.09	0.13
II, III	0.14	0.19	0.08	0.13	0.11	0.12
IV, V	0.12	0.23	0.40	0.27	0.38	0.37
VI, VII	0.20	0.10	0.23	0.18	0.14	0.27
VIII	0.34	–	0.08	–	0.04	–
9-R-Anthracene (starting)	0.04	0.38	0.07	0.36	0.14	0.19
t-BuOOH (starting)	0.07	0.03	1.47	1.75	–	–

[a] Average results.

with **I** under the given conditions. As the main products 9-methyl(phenyl)-9,10-dihydro-9,10-di-*tert*-butylperoxyanthracenes (**II, III**), 10-methyl(phenyl)-10-*tert*-butylperoxy-9-anthrones (**IV, V**), 10-hydroxy-10-methyl(phenyl)-9-anthrones (**VI, VII**) were isolated, while in the case of 9-MA also 9-methyl-10-hydro-9,10-epidioxyanthracene (**VIII**) was found (Table 1). The products of the reaction of the oxidation systems with the methyl group of 9-MA (9-anthraldehyde and 9-anthroic acid) were absent [Eq. (2)].



(2)

R = Me (**II, IV, VI, VIII**), Ph (**III, V, VII**).

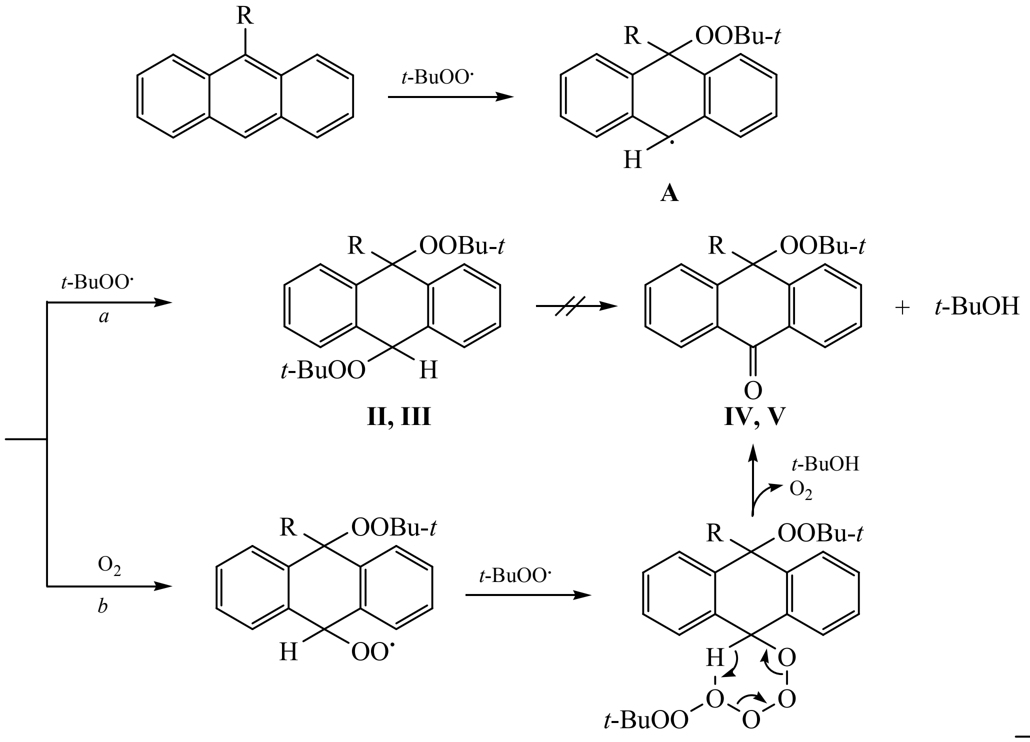
The presence of peroxides **II–V** points to the participation of *tert*-butylperoxy radicals in their synthesis. The latter can be formed either by the homolysis of trioxides [Eq. (1), route *b*] [1–6] or by the reaction of **I** with alkoxy radicals [Eq. (3)].

$$t\text{-BuOOH} + RO^{\cdot} \rightarrow t\text{-BuOO}^{\cdot} + ROH, \qquad (3)$$

$$R = t\text{-Bu}, [M].$$

The process of formation of diperoxides **II, III** can be represented by the scheme similar to that suggested earlier for 9,10-dimethyl-9,10-dihydro-9,10-di-*tert*-butylperoxyanthracene [11] and including in the first step the addition of t-BuOO$^{\bullet}$ radical to the system of conjugated bonds [Eq. (4), route *a*].

The consecutive reaction of peroxyradical **A** with oxygen generated by the system and with *tert*-



(4)

butylperoxy radicals via the stage of tetraoxide formation leads to the oxidation of the C–H bond in the position 10 and the formation of peroxyanthrones **IV, V** [Eq. (4), route *b*]. The assumed decomposition of compounds **II, III** does not occur. It was shown that on keeping the benzene solution of peroxide **II** for 20 days (20°C) the yield of *tert*-butanol does not exceed 2.5%.

Scheme (4) was proved by the reactions of 9-R-anthracenes with hydroperoxide **I** in the presence of di-*tert*-butylperoxalate (molar ratio 1 : 5 : 1, C_6H_6, 45°C). As the main products diperoxides **II, III** and peroxyanthrones **IV, V** were isolated (Table 2). As follows from the data of Table 2, in the presence of 9-alkyl (aryl)anthracenes the chain process of decomposition of hydroperoxide **I** [12] is practically fully suppressed. Even with a 5-fold molar excess of *t*-BuOOH with respect to peroxalate, from 40 to 60% of the hydroperoxide remains unconsumed. 9-R-Anthracenes act as acceptors of *tert*-butylperoxy radicals. Oxygen evolved upon decomposition and dimerization of *tert*-butylperoxy radicals oxidizes the C–H bond in the position 10 to the carbonyl group.

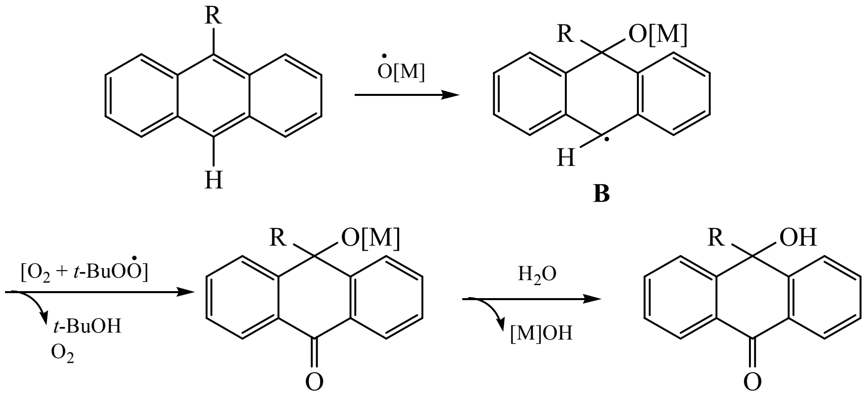
The third type of the products of oxidation of 9-R-anthracenes with the systems **I**–metal alkoxide are 10-hydroxy-10-methyl(phenyl)-9-anthrones (**VI, VII**) [Table 1] lacking in the reactions of these anthracenes with *t*-BuOOH in the presence of di-*tert*-butylperoxalate.

We believe that in the formation of hydroxyanthrones **VI, VII** metal-containing alkoxy radicals are involved, the products of homolysis of peroxytrioxides [Eq. (1)]. Metalalkoxy radicals can also be trapped by 9-substituted anthracenes to give radical **B**. Its further transformations by scheme (5) give rise to hydroxyanthrones **VI, VII**.

Table 2. Products of reaction of 9-R-anthracenes with *t*-BuOOH in the presence di-*tert*-butylperoxalate (molar ratio 1 : 5 : 1, C_6H_6, 45°C, 4 h, in moles per 1 mol of the substrate)

Reaction products[a]	R = Me	R = Ph
Me_2CO	0.02	0.02
t-BuOH	1.96	3.46
(t-BuO)$_2$	0.08	0.09
II, III	0.43	0.19
IV, V	0.28	0.62[b]
9-R-Anthracene (starting)	0.12	0.11
t-BuOOH (starting)	3.20	1.98

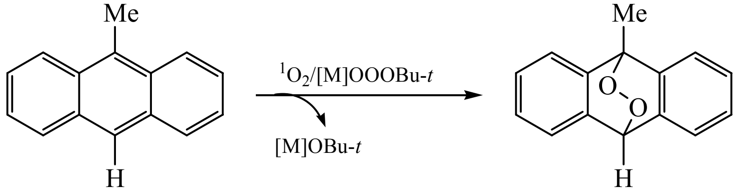
[a] Average results. [b] Also found 0.03 mol of anthraquinone.



(5)

[M] = Al(OBu-*t*)$_2$ [1], V(O)(OBu-*t*)$_2$ [4], Cr(O)(OBu-*t*)$_2$ [11].

The fourth product isolated from the reaction mixtures with 9-MA [Eq. (2)] is 9-methyl-10-hydro-9,10-epidioxyanthracene (**VIII**). The maximum yield of **VIII** (up to 35%) was obtained with aluminum alkoxide. The minimal amount of endoperoxide was detected in the system **I**–chromium alkoxide. The formation of peroxide **VIII** is indicative of the presence in the systems of either the singlet oxygen or metal-containing trioxides [M]OOOBu-*t* [1, 3, 11] [Eq. (6)]. No endoperoxide similar to **VIII** was found in the reactions of the oxidation systems with 9-phenylanthracene.



(6)

The composition of the products is the same for all the studied oxidation systems. However, the quantitative ratio depends both on the substituent in the anthracene molecule and on the nature of interaction of the metal alkoxide with hydroperoxide **I**. The 9-methylanthracene is more reactive, its degree of conversion is higher than that of 9-phenylanthracene. 9-Methylanthracene acts as an acceptor of the oxygen-centered radicals and singlet oxygen. In all reactions, along with *t*-BuOH, small amounts of acetone and *tert*-butylperoxide were isolated. In the presence of aluminum and chromium alkoxides, the conversion of hydroperoxide is practically total, whereas in the case of V(OBu-*t*)$_4$ the conversion of **I** does not exceed 65–70%.

Unlike the reaction with transition metal alkoxides, the reaction of 9-R-anthracenes with the system *t*-BuOOH–Al(OBu-*t*)$_3$ is followed by evolution of a large amount of oxygen 39, 57% respectively (Table 1), as well as by the formation of endoperoxide **VIII** (9-methylanthracene). This may be an indication of decomposition of the Al-containing peroxytrioxide [Eq. (1)] via molecular and homolytic routes in comparable degree.

The first step of the reaction of hydroperoxide **I** with vanadium and chromium alkoxides is their oxidation to oxo-derivatives by Eq. (7) [4, 6].

tert-Butoxy radicals can further react with hydroperoxide generating more *tert*-butylperoxy radicals. Tri-*tert*-butoxychromyl was identified in the volatile reaction products by the bands 250 and 371 nm in the electron absorption spectrum of the benzene solution [6].

The reaction of oxo-derivatives with *t*-BuOOH occurs both at the M–OBu-*t* bond by Eq. (1) with the formation and decomposition of peroxytrioxides and by the addition of hydroperoxide to the M=O group. The latter route in the case of chromium derivatives results

$$\mathrm{M(OBu\text{-}}t)_4 + t\text{-}\mathrm{BuOOH} \xrightarrow[t\text{-}\mathrm{BuOH}]{} [(t\text{-}\mathrm{BuO})_3\mathrm{MOOBu\text{-}}t] \longrightarrow \mathrm{O{=}M(OBu\text{-}}t)_3 + t\text{-}\mathrm{Bu}\dot{\mathrm{O}} \qquad (7)$$

in the liberation of water [6]. The amount of free oxygen does not exceed 10%, and the main mass of *t*-BuO groups attached to chromium is subjected to hydrolysis. As a result, precipitates insoluble in benzene and containing from 30 to 40% of chromium are formed. In the IR spectra of the precipitate the C–H and C–O vibration bands are lacking and bands at 3380 cm^{-1} appear assigned to stretching vibrations of the Cr–OH bond, 945 cm^{-1} typical of the Cr=O bond in chromyl [13], 817 cm^{-1} (Cr–O–Cr) and 1635 cm^{-1} (H_2O).

V–OBu-*t* bonds in $(t\text{-BuO})_4V$ are not hydrolyzed, no evolution of oxygen is observed and regardless of the reaction time (1–2 days) from 30 to 35% of hydroperoxide remain unconsumed. It should be noted that in the earlier studied reaction of $V(OBu\text{-}t)_4$ with *t*-BuOOH (1 : 10, C_6H_6, 25°C) the yield of oxygen did not exceed 50%. The presence of acetone and *tert*-butylperoxide is indicative of the homolytic nature of transformations [4]. Consequently, there must be routes preventing further formation of peroxytrioxides. As an option, it is presumable that the vanadium-containing peroxide not only reacts with hydroperoxide by Eq. (1) but is also decomposed to the monoalkoxy compound, which has low reactivity with respect to substitution of *tert*-butoxy group [Eq. (8)].

$$(t\text{-BuO})_3VO + t\text{-BuOOH} \xrightarrow[t\text{-BuOH}]{} (t\text{-BuO})_2V(O)OOBu\text{-}t \xrightarrow[2t\text{-BuO}^{\bullet}]{} t\text{-BuOVO}_2 \qquad (8)$$

The low yield of oxygen (if at all) and endoperoxide **VIII** in the case of vanadium and chromium alkoxides points to the predominant decomposition of peroxytrioxides by the homolytic route. As the main product of the reaction with catalytic amount of chromium alkoxide [9-PA : **I** : $Cr(OBu\text{-}t)_4$ = 10 : 60 : 1, 25°C, 3 days] peroxyanthrone **V** was isolated, which proves the predominant role of peroxyradicals.

All studied systems hydroperoxide **I**–metal alkoxide oxidize the C–H bonds of alkylarenes. The reactions have free-radical character, include the steps of formation of the C-centered radicals and their reaction with oxygen generated by the system. The C-centered and the peroxyradicals corresponding to them were detected by the ESR method as adducts with spin traps [1–6]. The processes of oxidation were assumed to be initiated by the O-centered radicals formed upon decomposition of metal-containing peroxytrioxides.

In order to prove the role of $RO^{\bullet}$ ($ROO^{\bullet}$) radicals in the processes of initiation we performed the reactions of 9-R-anthracenes with **I** in the presence of $Cr(OBu\text{-}t)_4$ (molar ratio 1 : 5 : 1) in solution in easily oxidizable hydrocarbon, ethylbenzene (Table 3). It is known that the main products of its oxidation by the system $Cr(OBu\text{-}t)_4$–*t*-BuOOH (25°C) are acetophenone, 1-phenyl-1-ethanol, 1-phenyl-1-*tert*-butylperoxyethane [6].

As follows from Table 3, the system **I**–$Cr(OBu\text{-}t)_4$ reacts both with ethylbenzene and with 9-R-anthracenes. All of the aforementioned oxidation products of the alkylarene, as well as diperoxides, peroxy- and hydroxyderivatives of the starting 9-R-anthracenes were isolated. The conversion of the latter is reduced almost three times relative to the similar process performed in benzene (Table 1). The yield of *tert*-butanol is substantially increased. The obtained data confirm the participation of alkoxy and peroxyradicals, the products of homolysis of metal peroxytrioxides, in the oxidation of alkylarenes. 9-R-Anthracenes act as acceptors of peroxyl and alkoxyradicals, which unequivocally proves the formation of the latter.

All compounds presented in Table 1 were isolated individually and characterized by the methods of IR, ^1H, ^{13}C NMR spectroscopy and by chemical transformations. There are no data in the literature on

Table 3. Products of the reaction of 9-R-anthracene with *tert*-butylhydroperoxide in the presence of chromium tetra-*tert*-butoxide (molar ratio 1 : 5 : 1, 20°C) in ethylbenzene (in moles per 1 mol of anthracene)

Reaction products	R = Me	R = Ph
t-BuOH	8.38	7.55
$(t\text{-BuO})_2$	0.04	0.06
PhC(O)Me	1.66	1.25
PhCH(OH)Me	Traces	0.33
PhCH(Me)OOBu-*t*	0.04	0.02
II, III	0.09	0.09
IV, V	0.21	0.05
VI, VII	0.13	0.18
VIII	0.04	–
9-R-Anthracene (starting)	0.37	0.60

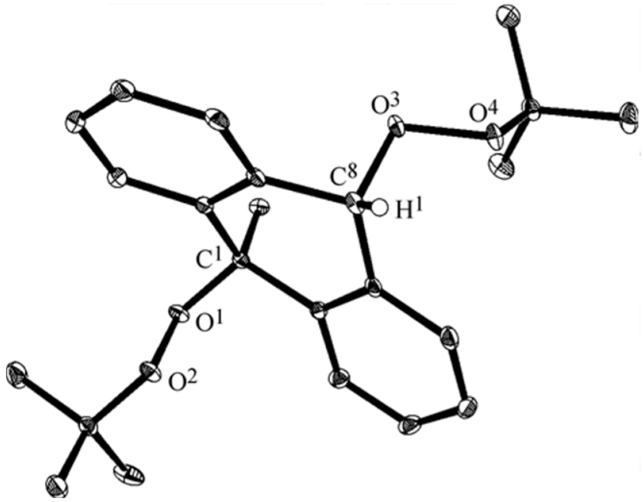


Fig. 1. Molecular structure of 9-methyl-9,10-dihydro-9,10-di-*tert*-butylperoxyanthracene (**II**).

diperoxides **II, III** or peroxyanthrone **V**. Endoperoxide **VIII** was obtained earlier by photocatalytic oxidation of 9-MA with oxygen in CD_3CN solution in the presence of 9-mesityl-10-methylacridinium [14]. The data of ^1H, ^{13}C NMR spectroscopy practically coincide with our data, other characteristics are lacking. The molecular structure of peroxides **II, III, V** as well as of endoperoxide **VIII** was determined by X-ray analysis (Figs. 1–4).

As can be seen from Figs. 1, 2, *tert*-butylperoxy groups in **II, III** are in the *trans*-configuration. The values of the bond distances and bond angles are typical for dialkylperoxides, close to those of di-*tert*-butylperoxide [15] (Table 4) and practically coincide with those of *trans*-9,10-dimethyl-9,10-dihydro-9,10-di-*tert*-butylperoxyanthracene [11]. The formation of the bridge structure of endoperoxide results in elongation of the O–O, C–O bonds and in the increase in the bond angles C–O–O.

All peroxyderivatives of 9-R-anthracenes, except for peroxyanthrone **IV**, have clearly defined melting points, which practically do not change after six months storage at 5°C. The decomposition of compounds **II, III, V** was performed at 140–150°C in sealed evacuated tubes both in the absence of solvent and in toluene. In all cases the formation of *t*-BuOH (0.83–0.88 mol), alcohols ROH (0.21–0.24 mol), acetone (0.11–0.18 mol), anthraquinone (0.12–0.55 mol) was demonstrated. Besides, poorly soluble in benzene residues of unidentified structure were found. Ethers ROBu-*t* are lacking among the products. The formation of anthraquinone can be represented by Eqs. (9)–(11).

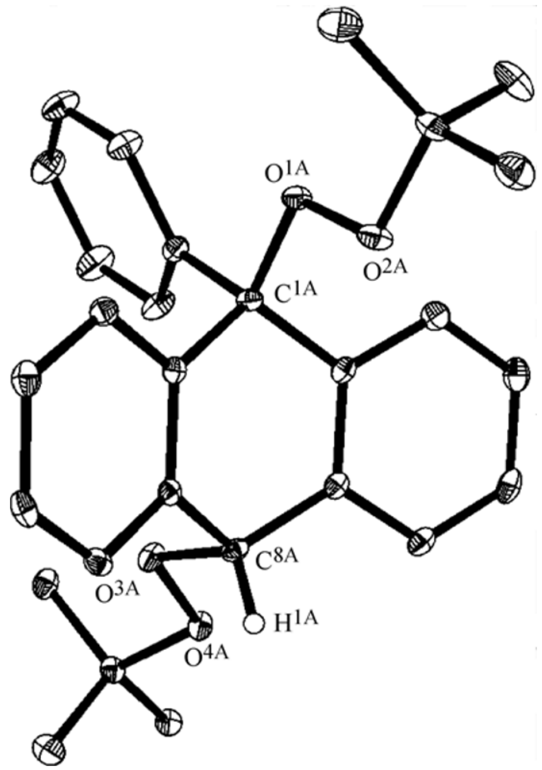


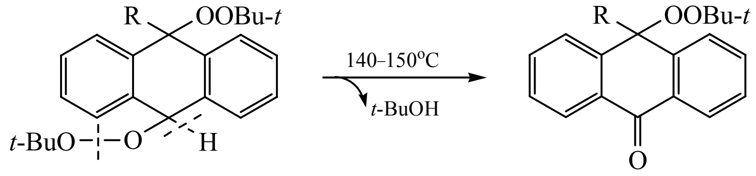
Fig. 2. Molecular structure of 9-phenyl-9,10-dihydro-9,10-di-*tert*-butylperoxyanthracene (**III**).

When carrying out the thermolysis in toluene solution the amount of *t*-BuOH was practically the same but 0.05–0.18 mol of *t*-BuOOH was detected. As the main products of decomposition of endoperoxide **VIII** (evacuated ampule, 150°C, 4 h) 9-MA (0.03 mol), anthraquinone (0.29 mol), 10-methylene-9-anthrone (0.19 mol) were identified.

Therefore, *tert*-butylhydroperoxide in the presence of metal *tert*-butoxides (M = Al, V, Cr) is an effective oxidant for 9-R-anthracenes.

EXPERIMENTAL

The reaction products were analyzed by the methods of GC, TLC, IR, UV, ^1H, and ^{13}C NMR spectroscopy. Electronic spectra were registered at room temperature on a UV-1800 (Shimadzu) instrument. IR spectra were recorded on an IR Prestige-21 (Shimadzu) instrument in KBr or in thin layer. NMR spectra were registered in $CDCl_3$ on an Agilent DD2 400 spectrometer at working frequencies 400 and 101 MHz respectively. Chemical shifts are given relative to Me_4Si.



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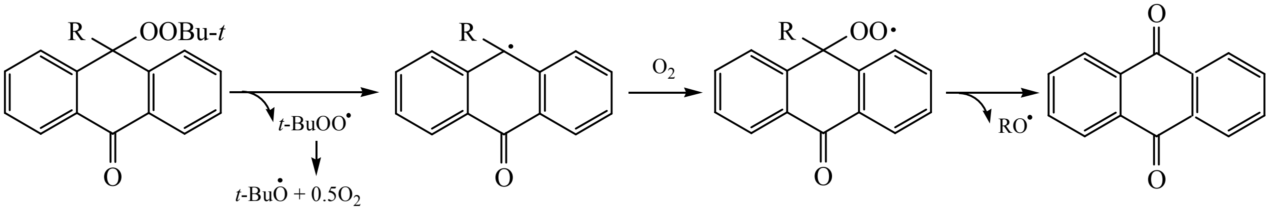

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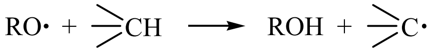

$$RO\cdot + {>}CH \longrightarrow ROH + {>}C\cdot$$

(11)

R = Me, Ph.

Chromatographic analysis of the reaction products in the liquid phase was performed on a GC-2010A (Shimadzu) instrument with a flame-ionization detector, gas carrier nitrogen, capillary column Equity-5, 30 m × 0.32 mm, ramp from 60 to 210°C. Calculations were performed by the method of external standard, using in each case authentic samples for comparison.

For isolation of the products of column chromatography separation silica gel 60, 0.06–0.2 mm (70–230 mesh) was used as adsorbent. Quantitative composition of the products and monitoring of the reactions was performed by TLC by comparing the R_f values of the sample and the reference compounds. Sorbent was Silpearl, a wide-porous silica gel on aluminum foil (Silufol UV-254) (eluent – benzene or benzene–petroleum ether (9 : 1), development with the solution of phosphorous-molybdenum acid on heating).

Qualitative analysis of hydroperoxides was performed by the method of iodometric titration. The amount of evolved oxygen was determined by the mass of benzoic acid formed upon the reaction of benzaldehyde with oxygen [16]. Chromium was determined by the Palmer method [17]. Carbonyl compounds were identified in the form of 2,4-dinitrophenylhydrazones.

X-ray analysis of compounds **II, III, V, VIII** was performed on Smart Apex I (**V**) and D8 Quest Photon

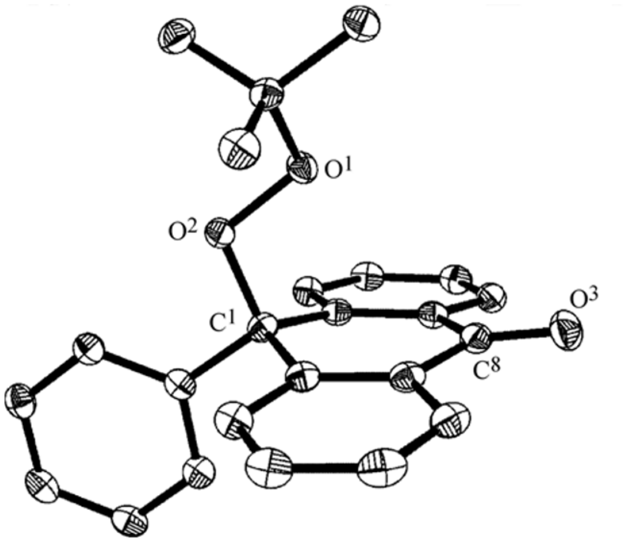

Fig. 3. Molecular structure of 10-phenyl-10-*tert*-butylperoxy-9-anthrone (**V**).

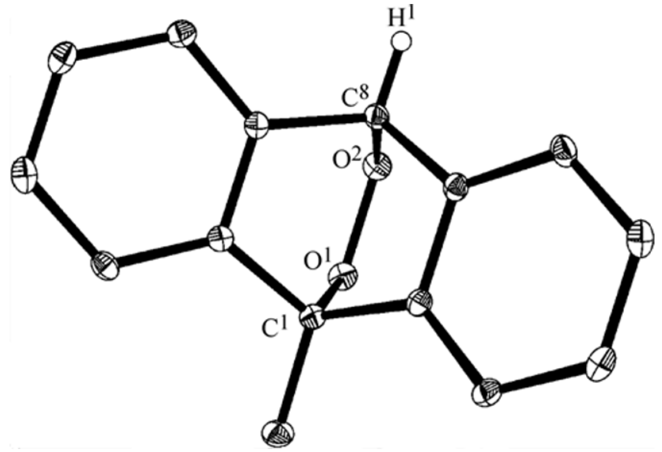

Fig. 4. Molecular structure of 9-methyl-10-hydro-9,10-epidioxyanthracene (**VIII**).

Table 4. Experimental geometrical parameters of *tert*-butyl-peroxyderivatives of 9-R-anthracenes

Parameter	Bond length, Å (angle, deg)				
	$(t\text{-BuO})_2$[a]	**II**	**III**[b]	**V**	**VIII**
$O^1–O^2$	1.478(3)	1.481(1)	1.477(1)	1.474(1)	1.491(1)
$O^3–O^4$		1.480(1)	1.486(1)		
$C^1–O$	1.439(4)	1.437(1)	1.432(1)	1.456(2)	1.479(1)
$C^8–O$		1.453(2)	1.443(1)	–	1.468(1)
C^1OO	106.7(2)	105.37(8)	106.77(6)	106.23(8)	111.46(7)
C^8OO		105.72(9)	105.62(7)	–	109.72(6)

[a] From [15]. [b] Geometrical parameters are given for one independent molecule.

(**II, III**, and **VIII**) diffractometers at 100K (MoK_α, graphite monochromator). The structures were solved by the direct method and refined by full-matrix least-squares method with respect to F^2 using the Shelxtl program package [18]. All nonhydrogen atoms were found from difference syntheses of electronic density and refined anisotropically. Hydrogen atoms were placed in the geometrically calculated positions and refined using the *rider* model. The extinction was taken into account by using the SADABS program [19]. Principal crystallographic data and details of measurements for compounds **II**, **III**, **V**, and **VIII** are presented in Table 5. The structures were deposited in the Cambridge Crystallographic Data Center (CCDC 1043804 for **II**, 1043805 for **III**, 1043806 for **V** and 1043807 for **VIII**).

Aluminum tri-*tert*-butoxide was prepared by the reaction of metal with *t*-BuOH and purified by sublimation at 150–160°C (1 mmHg). Found, %: Al 11.20. $C_{12}H_{27}AlO_3$. Calculated, %: Al 10.98. Vanadium tetra-*tert*-butoxide was synthesized from vanadium trichloride and lithium *tert*-butoxide [4], bp 89–90°C (1 mmHg) [20]. Chromium tetra-*tert*-butoxide was synthesized by the procedure [21]. Found, %: Cr 15.14. $C_{16}H_{36}O_4Cr$. Calculated, %: Cr 15.09. The spectral characteristics coincide with those in the literature [22].

10-Hydroxy-10-phenyl-9-anthrone was prepared by oxidation of 9-phenylanthracene with potassium bichromate [23], mp 215–216°C. Di-*tert*-butyl peroxalate was synthesized by treatment of oxalyl chloride with *tert*-butylhydroperoxide (99.5–99.8%) in the presence of pyridine, mp 50°C [24]. Commercial 9-methylanthracene (98%), 9-phenylanthracene (98%), 9-anthraldehyde (97%) (Aldrich) were used.

Reactions with metal alkoxides were carried out in dry, oxygen-free, argon atmosphere.

Reaction of 9-methylanthracene with *tert*-butylhydroperoxide in the presence of di-*tert*-butylperoxalate. The solution of 0.28 g of 9-methylanthracene, 0.32 g of di-*tert*-butylperoxalate and 0.63 g of *tert*-butylhydroperoxide (molar ratio 1 : 1 : 5) in 12 mL of benzene was placed in an ampule, degassed, sealed, and heated for 4 h at 45–47°C. After opening, in the ampule was detected 0.37 g of *t*-BuOOH. The ampule was sealed again and heated for another 6 h at the same temperature. Volatile components and solvent were condensed in a trap cooled with liquid nitrogen. In the condensate, 0.21 g of *t*-BuOH, 0.012 g of *tert*-butylperoxide and 0.36 g of *tert*-butylhydroperoxide was found. Hence, the reaction was complete after 4 h.

The residue after condensation was a dense viscous orange mass, from which two fractions were obtained by column chromatography (eluent – petroleum ether–diethyl ether, 9 : 1). After removal of solvent, the first fraction was chromatographed again, eluent – benzene. 0.029 g of unreacted 9-methylanthracene was isolated (78ºC) and 0.20 g of **9-methyl-9,10-dihydro-9,10-di-*tert*-butylperoxy-anthracene (II)**, yellow crystals, mp 75–76ºC. IR spectrum (KBr), ν, cm^{-1}: 3089, 2979, 2973, 2928, 1474, 1456, 1385, 1360, 1284, 1196, 1145, 1035, 973, 884, 762, 756, 606. ^{1}H NMR spectrum, δ, ppm: 1.10 s (9H), 1.25 s (9H), 1.68 s (3H), 5.82 s (1H), 7.32–7.79 (8H), 7.32 m (2H), 7.42 m (2H), 7.57 d (2H, *J* 7.6 Hz), 7.79 d (2H, *J* 7.8 Hz). ^{13}C NMR spectrum, δ_C, ppm: 26.60, 26.94 (CMe_3), 33.32 ($\underline{C}H_3$), 79.30, 80.27, 80.36 ($O\underline{C}\underline{Me}_3$, $Me\underline{C}O$), 81.51 ($H\underline{C}O$), 131.97, 143.53 (condensed rings), 125.16, 126.67, 128.49, 130.76 (Ph). Second fraction (0.085 g,

Table 5. Principal crystallographic data and refinement parameters for compounds **II**, **III**, **V**, and **VIII**

Parameter	Compound			
	II	**III**	**V**	**VIII**
Formula	$C_{23}H_{30}O_4$	$C_{28}H_{32}O_4$	$C_{24}H_{22}O_3$	$C_{15}H_{12}O_2$
M	370.47	432.54	358.42	224.25
Crystal system	Monoclinic	Triclinic	Monoclinic	Rhombic
Crystal system	*P*21/*c*	*P*-1	*P*21/*n*	*Pbca*
a, Å	10.1549(7)	10.4297(6)	9.2268(11)	7.4074(5)
b, Å	22.2492(15)	14.1450(8)	12.7903(15)	13.6139(8)
c, Å	9.6423(7)	16.4495(10)	16.2143(18)	21.7695(14)
α, deg	90	90.351(2)	90	90
β, deg	106.479(2)	103.331(2)	104.959(2)	90
γ, deg	90	90.102(2)	90	90
V, Å^3	2089.1(3)	2361.3(2)	1848.7(4)	2195.3(2)
Z	4	4	4	8
F(000)	800	928	760	944
d_{calc}, g/cm^3	1.178	1.217	1.288	1.357
μ, mm^{-1}	0.079	0.080	0.084	0.089
2θ range, deg	29.99	27.00	26.00	30.00
Measured reflections	29116	28819	15638	20239
Independent reflections (R_{int})	6077(0.0496)	10277(0.0246)	3636(0.0380)	3201(0.0633)
R_1 [$I > 2\sigma(I)$]	0.0560	0.0501	0.0425	0.0504
wR_2 (all data)	0.1333	0.1326	0.1197	0.1337
GOF	1.019	1.032	1.050	1.067
ρ_{max}/ρ_{min}, *e*/Å^3	0.504/–0.226	0.594/0.546	0.276/0.195	0.506/0.304

yellow dense oily liquid) was 10-methyl-10-*tert*-butylperoxy-9-anthrone (**IV**). The IR and ^{1}H, ^{13}C NMR spectra in $CDCl_3$ are identical to the published data [6]. Analysis on active oxygen was done as in [25] (70°C, sealed tube, 5 h). Found, %: O_{act} 5.28. $C_{19}H_{20}O_3$. Calculated, %: O_{act} 5.40. Compound **IV** slowly crystallized on staying but this is due to its decomposition to anthraquinone. The latter can be separated by dissolving **IV** in hexane. The analysis of peroxyanthrone **IV** by the NMR spectroscopy and on the active oxygen was performed during 1–2 days after isolation.

Reaction of 9-phenylanthracene with *tert*-butylhydroperoxide in the presence of di-*tert*-butylperoxalate (1 : 5 : 1). A mixture of 0.32 g of 9-phenylanthracene, 0.31 g of di-*tert*-butylperoxalate and 0.58 g of *tert*-butylhydroperoxide in 16 mL of benzene in an evacuated sealed ampule was heated for 6 h (45–47ºC). The solution was transparent, of lemon-yellow color. The condensate of volatile products contained 0.32 g of *t*-BuOH, 0.016 g of $(t\text{-BuO})_2$ and 0.22 g of *tert*-butylhydroperoxide. The residue was subjected to column chromatography (eluent is petroleum ether–Et_2O, 9.5 : 0.5) to get 2 fractions. From TLC data, the first fraction consisted of 2 substances, the second one was an individual compound. Repeated separation of the first fraction (eluent is benzene) gave 0.035 g of 9-PA (mp 153°C, no depression of the mixed probe) and 0.10 g of **9-phenyl-9,10-dihydro-9,10-di-*tert*-butylperoxyanthracene (III)** as colorless crystals, mp 137–138°C (decomp.). ^{1}H NMR spectrum, δ, ppm: 0.94 s

(9H), 1.24 s (9H), 5.89 s (1H), 7.08–7.23 m (3H), 7.29–7.44 m (6H), 7.65 d (2H, *J* 7.3 Hz), 7.75 d (2H *J* 7.8 Hz). ^{13}C NMR spectrum, δ_C, ppm: 26.44, 26.99, (CMe$_3$), 79.75, 80.12, 83.98 (O$\underline{C}$Me$_3$, Ph$\underline{C}$O), 80.53 (H$\underline{C}$O), 127.02, 127.17, 127.59, 127.77, 128.15, 128.29, 130.39, 133.23, 141.59, 144.64 (Ph, C_6H_4). After removal of solvent from the second fraction 0.28 g of **10-*tert*-butylperoxy-10-phenyl-9-anthrone** (**V**) was obtained as snow-white crystals, mp 135–136°C. IR spectrum (KBr), ν, cm^{-1}: 3068, 3034, 2982, 2928, 1662 (C=O), 1601 (C=C conjugated with C=O), 1446, 1322, 1362, 1193, 932 (*t*-Bu), 883 (*t*-BuO), 689, 757, 1588, 1156 (benzene rings). ^{1}H NMR spectrum, δ, ppm: 1.11 (9H, CMe$_3$), 7.14–8.31 (13H, Ph), 7.14–7.24 m (5H), 7.40–7.49 m (2H), 7.50–7.57 m (4H), 8.29–8.31 d (2H, *J* 7.7 Hz). ^{13}C NMR spectrum, δ_C, ppm: 26.76 (C$\underline{Me}_3$), 80.23 (C$\underline{Me}_3$), 81.71 (C$\underline{C}$O), 126.03, 126.79, 127.30, 128.06, 128.42, 129.13, 131.84, 133.24, 144.41, 145.40 (Ph, C_6H_4), 184.17 (CO). The predominant band is the band at 279.5 nm.

The presence of the carbonyl group was proved by the reaction with 2.4-dinitrophenyl-hydrazine. The treatment with NaI in acetic acid results in the formation of iodine. A specimen (55 mg), 0.5 g of NaI and 10 mL of glacial acetic acid was placed in an ampule, degassed and sealed. The ampule was heated at 90–95ºC for 8 h. For comparison, a blank experiment was done under the same condition. Found, %: O$_{act}$ 4.33. $C_{24}H_{22}O_3$. Calculared, %: O$_{act}$ 4.47.

Reaction of 9-methylanthracene with *tert*-butylhydroperoxide in the presence of Al(OBu-*t*)$_3$ (1 : 5 : 1). To 0.52 g of aluminum alkoxide in 20 mL of benzene the solution of 9-methylanthracene (0.41 g in 10 mL of benzene) was added, and then upon stirring 0.95 g of *t*-BuOOH was added by portions. The solution had pale-yellow color, which on the next day became dark-orange. After 2 days the solvent and volatile products were condensed in a trap cooled with liquid nitrogen. In the condensate, 0.88 g of *t*-BuOH, 5 mg of *t*-BuOOH and 5 mg of (*t*-BuO)$_2$ was found. The residue was hydrolyzed with 10% H_2SO_4 in ether, the ether layer was separated, water layer was extracted with ether. The ether extract was dried over Na_2SO_4, ether was removed, the residue was separated by column chromatography [eluent – benzene, benzene–Et$_2$O (~5%)] to give 5 fractions. The first fraction was unreacted 9-methylanthracene (0.015 g, mp 79°C), the second fraction was *trans*-diperoxide **II** (0.084 g). From the third fraction peroxyanthrone **IV** (0.11 g) was isolated. In the fourth fraction (0.11 g) **9-methyl-10-hydro-9,10-epidioxyanthracene (VIII)** was found as pale-yellow needle crystals, mp 128–129°C, decomp. above 135°C. IR spectrum (KBr), ν, cm^{-1}: 3057, 2978, 2933, 1461, 1373, 1192, 1078, 872, 775, 753, 726. ^{1}H NMR spectrum, δ, ppm: 2.16 s (3H, CH$_3$), 6.00 s (1H OCH), 7.28–7.30 m (4H), 7.40–7.43 m (4H). ^{13}C NMR spectrum, δ_C, ppm: 13.54 ($\underline{C}$H$_3$), 79.68, 80.10 (C$\underline{C}$O, H$\underline{C}$O), 120.97, 123.54, 127.78, 128.87, 138.55, 140.54 (C_6H_4). The compound readily forms iodine from NaI in acetic acid. To complete the reaction, the solution was heated for 2 h at 60ºC. For comparison, a blank experiment was done under the same condition. Found, %: O$_{act}$ 7.22. $C_{15}H_{12}O_2$. Calculated, %: O$_{act}$ 7.13.

From the fifth fraction, 10-methyl-10-hydroxy-9-anthrone [(0.094 g), mp 152–153ºC (from cyclohexane)] [23, 26] was isolated. The data of IR and ^{1}H, ^{13}C NMR spectroscopy are identical to those in the literature [26]. The amount of oxygen in each separate experiment was determined by the known procedure [16].

Reaction of 9-phenylanthracene with *t*-BuOOH in the presence of Cr(OBu-*t*)$_4$ (1 : 5 : 1). To the solution of 0.40 g of Cr(OBu-*t*)$_4$ and 0.30 g of 9-PA in 15 mL of benzene 0.53 g of *t*-BuOOH in 2 mL of C_6H_6 was gradually added upon stirring. The blue color of the alkoxide rapidly turned red-cherry and dark-brown precipitate was formed. Evolution of oxygen was not active and finished in several minutes. After 2 days, the solvent was condensed into a trap and it was found to contain 5 mg of acetone, 0.59 g of *t*-BuOH, 21 mg of (*t*-BuO)$_2$. The residue, dark-brown solid, was hydrolyzed in ether with 10% sulfuric acid, extracted with ether, the extract was dried over Na_2SO_4 and analyzed by the method of column chromatography (eluent – benzene). The TLC analysis showed that the ether extract contained four main products. The first fraction was the unreacted 9-PA, mp (and of the mixed probe) 152–153ºC. From the second and third fractions diperoxide **III** (0.05 g) and peroxyanthrone **V** (0.16 g) were isolated. Their melting points, IR and NMR spectra were identical to those of the products of the reaction of 9-PA with *t*-BuOOH and DTBPO. The fourth fraction (0.09 g) was **10-hydroxy-10-phenyl-9-anthrone** (**VII**), white-snow crystals from chloroform, mp 214–215ºC, give violet color with conc. H_2SO_4 [23, 26]. The data of IR, NMR spectroscopy of hydroxyanthrone **VII** isolated from the reaction and independently synthesized were identical and in general corresponded to the literature data [26]. ^{1}H NMR spectrum, δ, ppm: 3.08 s (1H, OH), 7.13–7.61 (11H, 7.13–7.16 m (1H), 7.21–7.24 t (2H, *J* 7.5 Hz), 7.33–7.35 d (2H, *J* 7.7 Hz) 8.20–8.22 d (2H, *J* 7.8 Hz). ^{1}H NMR spectrum from [26], δ, ppm: 2.18 s (1H), 7.1–7.7 m (11H), 8.2–8.4 m (2H).

In some experiments in the reactions of 9-MA and 9-PA with *t*-BuOOH in the presence of Cr(OBu-*t*)$_4$ the insoluble dark-brown precipitate was separated, washed with benzene, dried and analyzed for the content of chromium, which was from 30 from 39%. The condensate of volatile products of bright-yellow color was treated with triphenylphosphine. Disappearance of the color was indicative of the presence of compounds with the Cr=O bond in the benzene solution [13].

The experiments and analysis of the products of the reactions of 9-MA and 9-PA with hydroperoxide **I** in the presence of metal alkoxides not mentioned above was performed similarly.

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