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Reactions of Hydroxyl-Containing Compounds with *tert*-Butyl Hydroperoxide in the Presence of Chromium Tetra-*tert*-butoxide

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Abstract—Primary and secondary aliphatic, alkylaromatic, cyclic, and organoelement alcohols are efficiently oxidized by *tert*-butyl hydroperoxide in the presence of both equimolar and catalytic quantities of chromium tetra-*tert*-butoxide (C_6H_6, 20°C). α-Diols containing tertiary hydroxyl groups interact with this system via oxidative splitting of the carbon scaffold. The oxidation includes the stages of formation and decomposition of chromium-containing peroxy compounds. Further transformations of the carbonyl compounds depend on the structure of radicals in the molecules.

Keywords: chromium tetra-*tert*-butoxide, *tert*-butyl hydroperoxide, oxidation, hydroxyl-containing compound, primary alcohol, secondary alcohol, pinacol, 3,6-di-*tert*-butylcatechol

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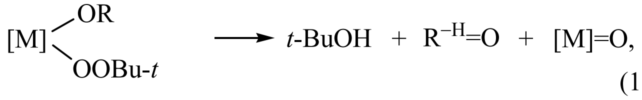
Systems based on *tert*-butyl hydroperoxide **1** in combination with aluminum [1], titanium [2], or vanadium *tert*-butoxides [3] efficiently oxidize secondary alcohols under mild conditions (20°C); the oxidation of primary alcohols is less efficient. The reactions proceed via the intermediate formation and decomposition of peroxy compounds containing the alcohol residue as one of the alkoxy groups [Eq. (1)].



$$[\mathrm{M}]\begin{matrix}\diagup\mathrm{OR}\\ \diagdown\mathrm{OOBu}\text{-}t\end{matrix} \longrightarrow t\text{-BuOH} + \mathrm{R}^{-\mathrm{H}}{=}\mathrm{O} + [\mathrm{M}]{=}\mathrm{O}, \tag{1}$$

$$\mathrm{M} = \mathrm{Al, Ti, V}.$$

We have earlier demonstrated the possibility of alcohols oxidation by hydroperoxide **1** in the presence of chromium tetra-*tert*-butoxide **2** [4]. The reaction of the components in the equimolar ratio (C_6H_6, 20°C) leads to oxidation of alkoxide **2** into chromyl [Eq. (2)].

$$(t\text{-BuO})_4\mathrm{Cr} + t\text{-BuOOH} \xrightarrow[-t\text{-BuOH}]{} (t\text{-BuO})_3\mathrm{CrOOBu}\text{-}t \longrightarrow (t\text{-BuO})_3\mathrm{Cr}^{+5}{=}\mathrm{O} + t\text{-BuO}^{\bullet}. \tag{2}$$

Increase of the reagents ratio up to 2 : 1 or higher results in evolution of oxygen, its yield attaining 65%. The occurring processes include the formation of chromium-containing peroxides and peroxy trioxides that are further decomposed via evolution of oxygen (including that in the singlet state) and via formation of oxygen-centered alkoxy and peroxy radicals [Eq. (3)] [4].

$$[\mathrm{Cr}]\mathrm{OBu}\text{-}t \xrightarrow[-t\text{-BuOH}]{t\text{-BuOOH}} [\mathrm{Cr}]\mathrm{OOBu}\text{-}t \xrightarrow[-t\text{-BuOH}]{t\text{-BuOOH}} [\mathrm{Cr}]\mathrm{OOOBu}\text{-}t$$

$$\begin{cases} \xrightarrow{a} {}^1\mathrm{O}_2,\, {}^3\mathrm{O}_2 + [\mathrm{Cr}]\mathrm{OBu}\text{-}t, \\ \xrightarrow{b} [\mathrm{Cr}]\mathrm{O}^{\bullet} + {}^{\bullet}\mathrm{OOBu}\text{-}t + [\mathrm{Cr}]\mathrm{OO}^{\bullet} + {}^{\bullet}\mathrm{OBu}\text{-}t. \end{cases} \tag{3}$$

Table 1. Products of oxidation of primary alcohols (RCH_2OH) by the *t*-BuOOH–Cr(OBu-*t*)$_4$ system (benzene, 20°C, mol/mol of alcohol)

Reaction products	*n*-$PrCH_2OH$		*t*-$BuCH_2OH$		Me_3SiCH_2OH		$PhCH_2OH$	
	1 : 3 : 1[a]	10 : 30 : 1[a]	1 : 3 : 1[a]	10 : 30 : 1[a]	1 : 3 : 1[a]	10 : 30 : 1[a]	1 : 3 : 1[a]	10 : 30 : 1[a]
Carbonyl compounds	PrCHO[b]		*t*-BuCHO		$(Me_3Si)_2O$		PhCHO	
	0.16	Traces	0.15	0.01	0.30	0.10 + Me_3SiOH 0.48	0.70	0.38
Carboxylic acid	PrCOOH		*t*-BuCOOH		$Me_3SiCOOH$		PhCOOH	
	0.53	0.38	0.61	0.44	0.21	–	0.28	0.60
Ester	$PrCOOCH_2Pr$		*t*-$BuCOOCH_2Bu$-*t*		$Me_3SiOCH_2SiMe_3$		$PhCOOCH_2Ph$	
	0.01	Traces	Traces	0.01	–	0.22	0.02	0.01
t-BuOH	5.73	2.37	5.86	3.12	5.98	1.91	6.07	1.70
t-BuOOBu-*t*	0.03	0.05	0.11	0.14	0.04	0.03	0.04	0.07
Acetone	0.01	0.04	0.03	0.04	–	–	0.02	0.05
ROH (init.)	0.02	0.38	0.12	0.41	–	–	–	–
t-BuOOH (init.)	–	0.02	–	0.19	0.08	1.30	–	–

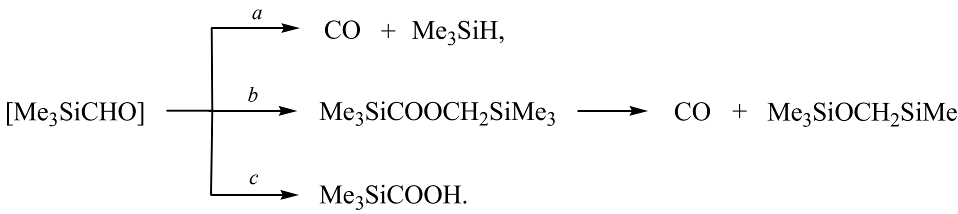
[a] The ROH : *t*-BuOOH : Cr(OBu-*t*)$_4$ molar ratio. [b] Products of condensation of butanal were also detected.

The formation of *t*-BuO$^{\cdot}$ and *t*-BuOO$^{\cdot}$ radicals has been confirmed by the presence of acetone and *tert*-butyl peroxide in the mixture.

In the present work we studied the reaction of the *t*-BuOOH–Cr(OBu-*t*)$_4$ system with various hydroxyl-containing compounds, aiming to elucidate the effect of the radical nature on the conversion of the substrate, the structure of the formed products, and their further transformations. Aliphatic, aromatic, cyclic and, organoelement alcohols were used as the objects. Benzene used as the reaction medium was not oxidized under the reaction conditions (20°C). The alcohol to the hydroperoxide molar ratio was always of 1 : 3. The hydroperoxide to alkoxide **2** ratio was varied from 3 : 1 to 30 : 1. In the latter case, Cr(OBu-*t*)$_4$ acted as catalyst with respect to *t*-BuOOH, allowing for additional route of oxygen generation via decomposition of the hydroperoxide induced by alkoxy radicals [Scheme (3)].

The data on the reaction of the primary alcohols with hydroperoxide **1** in the presence of alkoxide **2** are given in Table 1. Benzyl alcohol and trimethylsilylmethanol reacted quantitatively both at the equimolar and the catalytic content of alkoxide **2**. The conversion of aliphatic alcohols did not exceed 60%, being the highest at the reagents ratio of 1 : 3 : 1. The major products were aldehydes and the corresponding carboxylic acids. When equimolar amount of alkoxide **2** was used, aldehydes were the major products.

In the case of trimethylsilylmethanol as substrate, the set of the formed products was more complex. Aldehydes of the R_3SiCHO type are known to be unstable. However, the nature of the isolated products (Table 1) suggested the formation of trimethylformylsilane as the intermediate; it was further decomposed following scheme (4), the *a* route being predominant.



(4)

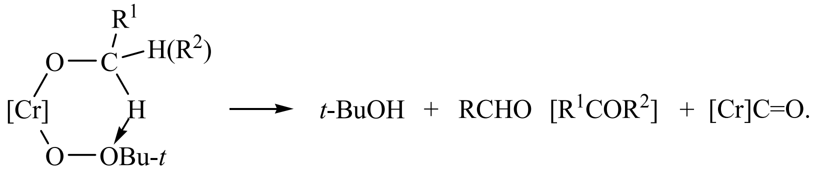
Under the reaction conditions, trimethylsilane was oxidized into trimethylhydroxysilane, which existed predominantly in the free state in the presence of catalytic amount of the alkoxide. The chromium compounds promoted its dehydration into hexamethylsiloxane observed at the equimolar ratio of Me_3SiCH_2OH and **2**. We assume that peroxy compounds of chromium act as oxidizer in the reaction; however, we did not establish the nature of the oxidant unambiguously.

$$Me_3SiH + [Cr]OOBu\text{-}t \longrightarrow Me_3SiOH + [Cr]OBu\text{-}t. \quad (5)$$

The formation of trimethylsilyltrimethylsiloxymethane could be explained by decarbonylation of the ester (the product of the aldehyde condensation). Similar compounds have been earlier identified in the reaction of bis(trimethylsilylmethoxy)aluminum bromide with *t*-BuOOH [5].

The *t*-BuOOH–$Cr(OBu\text{-}t)_4$ system was efficient in oxidation of secondary alcohols under mild conditions (C_6H_6, 20°C). The structure of the substituent at the carbon atom bearing the alcohol group had practically no effect on the yield of ketones (Table 2). Aliphatic, alkylaromatic, and cyclic ketones were formed in yield of 75–100%. For example, transformation of *D,L*-borneol into camphor was quantitative. Methyl ester of pyruvic acid was formed from methyl lactate in up to 80% yield irrespectively of the molar ratio of the reagents.

The results led to assumpsion that the chromium peroxides acted as the alcohol oxidants. They could be formed either via the exchange of the *tert*-butoxy radical in the $(t\text{-}BuO)_3CrO$ chromyl with the *tert*-butylperoxy group $[(t\text{-}BuO)_2Cr(O)OOBu\text{-}t]$ or via addition of hydroperoxide at the Cr=O bond $[(t\text{-}BuO)_3Cr(OH)\cdot OOBu\text{-}t]$ [6–8]. Replacement of the second *tert*-butoxy group with the alcohol should have led to the alkoxy chromium derivative that was decomposed to form the carbonyl compound [Eq. (6)].



(6)

Regeneration of the catalyst at the 10 : 30 : 1 ratio of the reagents occurred following scheme (7), similar to oxidation of alcohols with hydroperoxide **1** in the presence of CrO_3 [6–8].

$$[Cr]{=}O + t\text{-}BuOOH \longrightarrow [Cr](OH)OOBu\text{-}t \xrightarrow[-H_2O]{ROH} [Cr](OR)OOBu\text{-}t. \quad (7)$$

Hydrolysis of the *t*-BuO[Cr] bonds with water resulted in precipitation of chromium inorganic compounds exhibiting the IR absorption bands at 3300 cm^{-1} (CrOH) as well as 515 and 805 cm^{-1} (CrOCr).

The data collected in Tables 1 and 2 suggested that aldehydes and ketones underwent further transformations, depending on the structure of the substituents at the carbonyl group. We identified the products of the aldol condensation of butanal and methyl ethyl ketone. A substantial part of aldehydes was converted into carboxylic acids. In order to better understand the process, we studied oxidation of benzaldehyde at various ratios of the reagents (Table 3). Both oxygen generated by the system [4] and the chromium-containing peroxides could act as oxidant. The latter case was most probable at the PhCHO : *t*-BuOOH ratio of 1 : 2 and 1 : 3 [Eq. (8)].

$$PhCHO + [Cr]OOBu\text{-}t \longrightarrow t\text{-}BuOH + [Cr]OCOPh. \quad (8)$$

The major fraction of the acid existed in the form of the salt and was isolated after hydrolysis with 10% H_2SO_4. When the reaction was performed in the catalytic regime, the aldehyde was quantitatively converted into the acid, existing in solution in the free state. Apparently, in that case the homolytic process of PhCHO oxidation with oxygen generated by the system took place as well.

The decrease of the benzyl phenyl ketone yield (Table 2) was due to its further reaction with the oxidative system leading to the splitting of the carbon scaffold of the starting alcohol. Oxidation of on the benzyl fragment of PhCOBn should have led to benzoin and dibenzoyl [4]. However, functionalization of the alcoholic hydroxyl group of benzoin could be accompanied by the reaction of its carbonyl group with

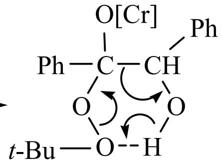
Table 2. Products of oxidation of secondary alcohols (ROH) by the *t*-BuOOH-Cr(OBu-*t*)$_4$ system (benzene, 20°C, mol/mol of alcohol)

Reaction products	*s*-BuOH		PhCH(OH)Me		PhCH(OH)CH$_2$Ph			*D,L*-borneol		MeCH(OH)COOMe	
	1 : 3 : 1[a]	10 : 30 : 1[a]	1 : 3 : 1[a]	10 : 30 : 1[a]	1 : 3 : 1[a]	1 : 6 : 1[a]	10 : 30 : 1[a]	1 : 3 : 1[a]	10 : 30 : 1[a]	1 : 3 : 1[a]	10 : 30 : 1[a]
Carbonyl compounds	MeCOEt[b]		PhCOMe		PhCOCH$_2$Ph			Camphor		MeC(O)COOMe	
	0.77	0.83	0.95	0.75	0.74	0.83	0.85	0.97	1.00	0.77	0.78
					PhCOCOPh						
					0.06	0.02	0.08				
					PhCHO						
					0.14	0.15	0.02				
					PhCOOH[c]						
					0.10	0.12	–				
t-BuOH	5.37	2.68	5.92	2.30	5.10	7.11	2.15	5.53	3.03	6.15	2.00
t-BuOOBu-*t*	–	0.04	0.02	0.05	0.07	0.18	0.04	0.07	0.07	0.02	0.06
Acetone	0.01	0.03	–	0.03	0.05	0.04	–	0.02	0.04	0.06	0.07
ROH (init.)	0.10	–	–	0.17	–	–	–	0.01	–	0.23	0.21
t-BuOOH (init.)	–	0.12	–	0.15	–	0.03	0.13	–	–	–	0.59

[a] The ROH : *t*-BuOOH : Cr(OBu-*t*)$_4$ molar ratio. [b] Products of condensation of methyl ethyl ketone were also detected. [c] Found 0.02–0.05 mol of *tert*-butyl benzoate and traces of benzyl benzoate.

t-BuOOH or chromium-containing peroxide yielding α-hydroxyperoxide. Intramolecular decomposition of the latter should have afforded benzoyloxychromium and benzaldehyde or benzoic acid [Eq. (9)].

$$\mathrm{PhCOCH(OH)Ph} + [\mathrm{Cr}]\mathrm{OOBu}\text{-}t \longrightarrow$$



$$\longrightarrow [\mathrm{Cr}]\mathrm{OC(O)Ph} + \mathrm{PhCHO} + t\text{-}\mathrm{BuOH}. \qquad (9)$$

Table 3. Products of the reaction of benzaldehyde with the *t*-BuOOH–Cr(OBu-*t*)$_4$ system (benzene, 20°C, mol/mol of aldehyde)

Molar ratio of the reagents	1 : 2 : 1[a]	1 : 3 : 1[a]	10 : 30 : 1[a]
PhCOOH	0.70	0.76	0.98
t-BuOH	4.87	6.50	2.86[b]
t-BuOOBu-*t*	0.02	0.06	0.03
PhCHO (init.)	0.22	0.21	Traces

[a] The PhCHO : *t*-BuOOH : Cr(OBu-*t*)$_4$ molar ratio. [b] Found 0.85 mol of unreacted hydroperoxide **1**.

The suggested pathway was confirmed by carrying out the reactions of benzoin with the oxidative system at the molar ratios given in Table 2. As expected, dibenzoyl was isolated as the major product (0.75–0.80 mol). Benzaldehyde (~0.05 mol) and PhCOOH (0.12–0.15 mol) were identified as well.

Hence, *tert*-butyl hydroperoxide in the presence of chromium tetra-*tert*-butoxide was an efficient oxidizer of primary and secondary alcohols under mild conditions (20°C). Chromium alkoxide could be used either in equimolar or catalytic amount with respect to the hydroperoxide.

Since oxidation of the R$_3$COH tertiary alcohols occurred only under very severe conditions and was accom-

Table 4. Products of oxidation of α-diols by the *t*-BuOOH–Cr(OBu-*t*)$_4$ system (benzene, 20°C, mol/mol of alcohol)

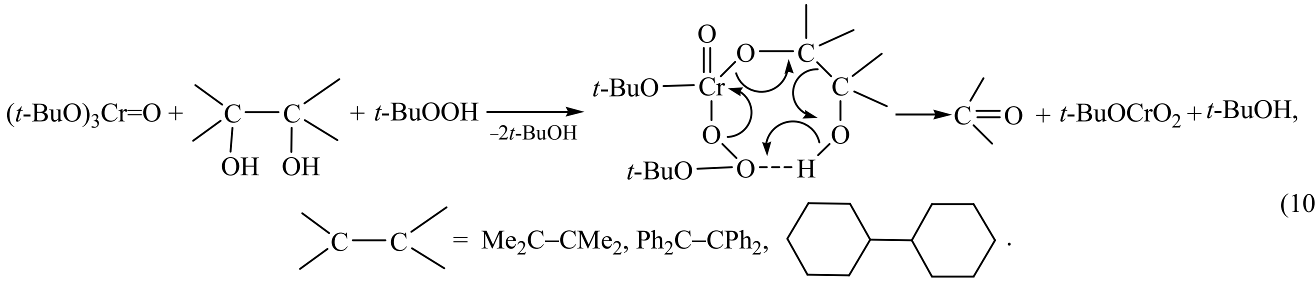
Reaction products	Tetramethylethanediol		1,1-Dioxydicyclohexyl		Tetraphenylethanediol		Triphenylethanediol		3,6-Di-*tert*-butylcatechol	
	1 : 3 : 1[a]	10 : 30 : 1[a]	1 : 3 : 1[a]	10 : 30 : 1[a]	1 : 3 : 1[a]	10 : 30 : 1[a]	1 : 3 : 1[a]	10 : 30 : 1[a]	1 : 3 : 1[a]	10 : 30 : 1[a]
Carbonyl compounds	Acetone		Cyclohexanone		Benzophenone		Benzophenone		3,6-Di-*tert*-butyl-*o*-benzoquinone	
	1.53	0.90	1.26	1.37	0.87	0.68	0.98	0.80	0.33[b]	0.75[c]
							Benzaldehyde			
							0.46	0.52		
							Benzoic acid			
							0.48	0.27		
t-BuOH	7.29	3.67	5.98	3.40	5.87	2.49	8.10	3.04	7.22	2.74
t-BuOOBu-*t*	0.09	0.15	0.10	0.13	0.08	0.11	0.07	0.05	0.03	0.01
Acetone			0.03	–	0.20	Traces	Traces	–	0.06	–
α-Diol (init.)	0.20	0.49	0.15	0.27	0.46	0.62	–	Not detected	0.40	Traces
t-BuOOH (init.)	–	–	–	–	–	1.10	–	0.43	–	1.04

[a] The α-diol : *t*-BuOOH : Cr(OBu-*t*)$_4$ molar ratio. [b] Also found: 2-hydroxy-3,6-di-*tert*-butyl-*p*-benzoquinone (0.07 mol), 3,6-di-*tert*-butyl-3,6-di-*tert*-butylperoxycyclohexene-4-dione-1,2 (0.02 mol), 5-hydroxy-3,6-di-*tert*-butyl-2,3-epoxy-*p*-benzoquinone (0.01 mol). [c] Also found: 2-hydroxy-3,6-di-*tert*-butyl-*p*-benzoquinone (0.05 mol), 3,6-di-*tert*-butyl-3,6-di-*tert*-butylperoxycyclohexene-4-dione-1,2 (0.11 mol), 5-hydroxy-3,6-di-*tert*-butyl-2,3-epoxy-*p*-benzoquinone (0.02 mol).

panied by the rupture of the C–C bonds, we investtigated the reaction of the studied system with several α-diols containing tertiary hydroxyl groups: pinacols, secondary-tertiary α-diol, and a diatomic phenol (Table 4). The reactions were also carried out in benzene (20°C) at the α-diol : *t*-BuOOH : Cr(OBu-*t*)$_4$ ratio of 1 : 3 : 1 or 10 : 30 : 1. The conversion of pinacols decreased when catalytic amount of alkoxide **2** was used.

Using *trans*-1,1-dioxydicyclohexyl as an example, we showed that the reaction with Cr(OBu-*t*)$_4$ (1 : 1, C_6H_6, 20°C) occurred at the both hydroxyl groups and was accompanied by evolution of two moles of *t*-BuOH. Formation of the glycolate derivative of that pinacol was prevented due to the steric factors; therefore, alkoxy groups of different alkoxide molecules participate in the reaction. The same should have been true for benzpinacol. The chromium atom retained its degree of oxidation of +4 in those reactions, as confirmed by no change of the mixture color [9]. The formed derivatives were stable and did not give products of pinacols splitting 50–60°C.

When all the three components were mixed together, the color changed from bright blue into yellow-orange, and the precipitate of inorganic chromium compounds was formed. The products of destructive oxidation of tetramethylethanediol, 1,1-dioxydicyclohexyl, and benzopinacol were isolated after the reaction (Table 4). We believe that pinacol (via one of the OH groups) and the hydroperoxide interacted simultaneously with the chromium alkoxide, to form the alkoxy derivative via oxidative splitting of the C–C bond of pinacol [Eq. (10)].



(10)

Similar oxidation reactions of α-diols have been observed earlier for the $Zr(OBu\text{-}t)_4$–t-BuOOH system [10].

Oxidative decomposition of triphenylethanediol $Ph_2C(OH)CH(OH)Ph$ led to the formation of benzophenone and benzaldehyde, the latter being further converted to benzoic acid under the reaction conditions. The substrate conversion was of ≈100% at the 1 : 3 : 1 reagents ratio and of 80% when catalytic amount of **2** was used.

Since triphenylethanediol contained secondary hydroxyl group at the benzylic carbon atom, it could be converted into ketoalcohol $Ph_2C(OH)C(O)Ph$ at the first stage and then react with chromium peroxy derivative [similarly to benzoin, Eq. (9)]. However, in that case benzoic acid should have been exclusively formed along with benzophenone; therefore, in practice the reaction followed Eq. (10). The presence of sterically less hindered and more acidic benzylic hydroxyl favored the conversion of the diol.

3,6-Di-*tert*-butylcatechol **3** was oxidized into 3,6-di-*tert*-butyl-*o*-benzoquinone **4** in the presence of the **1–2** system under mild conditions (Table 4); the product yield was of 0.75 mol when the reaction was performed under the catalytic conditions. On top of that, 2-hydroxy-3,6-di-*tert*-butyl-*p*-benzoquinone and 3,6-di-*tert*-butylperoxycyclohexen-4-dione-1,2 were detected as the products. The TLC analysis revealed the presence of small amounts of several unidentified products and traces of catechol **3** as well.

Apparently, the conversion of catechol **3** into quinone **4** occurred according to Eq. (10) via the eight-membered transition state involving the π-system of the benzene ring. The scheme involving the metal monoalkoxy derivative has been earlier suggested for oxidation of catechols into quinones by *tert*-butylhydroperoxide in the presence of ruthenium salts [11] and for oxidation of 3,6-di-*tert*-butylcatechol into quinone by the hydroperoxide **1**–aluminum, titanium, or zirconium *tert*-butoxide systems [12]. Validity of the equation similar to Eq. (10) was proved by the reaction of catechol **3** with di-*tert*-butoxy-*tert*-butylperoxyaluminum (1 : 1, C_6H_6, 20°C) yielding 0.75 mol of quinone **4**. However, we could not completely rule out the formation of quinone via the homolytic reaction of catechol **3** with the radicals generated by the used system, especially when catalytic amounts of **2** were used. When the reaction was carried out at the **3** : **1** : **2** ratio of 1 : 3 : 1, the yield of quinone **4** did not exceed 33%. We assumed that the latter was involved in further transformations (Table 4).

The hydroperoxide **1**–aluminum, titanium or zircon-nium *tert*-butoxide systems are known to oxidize quinone **4** [(2 : 1 : 1), C_6H_6, 20°C] with preservation of the carbon scaffold of the latter. The major reaction products are 2-hydroxy-3,6-di-*tert*-butyl-*p*-benzoquinone **5** in the case of $Ti(OBu\text{-}t)_4$ and 5-hydroxy-3,6-di-*tert*-butyl-2,3-epoxy-*p*-benzoquinone **6** in the cases of $Zr(OBu\text{-}t)_4$ or $Al(OBu\text{-}t)_3$ [12]. The yield of the latter in the reaction with $Al(OBu\text{-}t)_3$ reaches 95%. Later, we have shown that similar systems, hydroperoxide **1**–*tert*-butoxy derivatives of vanadium [$(t\text{-}BuO)_4V$ or $(t\text{-}BuO)_3VO$] react with quinone **4** (3 : 1 : 1) predominantly via destruction of the molecule scaffold. 3,6-Di-*tert*-butyl-2-pyrone **7** (0.30 mol) and 3,6-di-*tert*-butyl-1-oxacyclohepta-3,5-diene **8** (0.37–0.40 mol) have been isolated along with hydroxyquinone **5**. In all the cases, the metal-containing peroxides act as oxidants.

In view of the above, the nature of the products of the **4** reaction with the *tert*-butyl hydroperoxide–metal alkoxide system depends on the metal derivative nature. Hence, we investigated the reaction of quinone **4** with the hydroperoxide **1**–chromium tetra-*tert*-butoxide system as well as with the earlier studied t-BuOOH–cobalt acetylacetonate system [13] (C_6H_6, 20°C).

The reaction of di-*tert*-butyl-*o*-benzoquinone with the **1–2** system at the reagents molar ratios of 1 : 3 : 1 and 1 : 5 : 1 occurred within 1–2 days and was accompanied by evolution of CO. The following compounds were found in the condensate of the volatile products [mol/mol of quinone **4**]: acetone (0.03–0.05), *tert*-butylperoxide (0.08–0.10), methyl *tert*-butyl ether (≈0.05), and t-BuOH (6.22–7.00). It was shown that the products that appeared predominant in the reaction of quinone oxidation with hydroperoxide **1** in combination with aluminum, titanium, zirconium, and vanadium alkoxides [namely, hydroxyquinone **5**, epoxyquinone **6**, anhydride **8**, and pyrone **7**] were formed in the studied reaction as well, their amount being of 0.02–0.05 mol. The earlier unknown 3,6-di-*tert*-butyl-3,6-di-*tert*-butylperoxycyclohexene-4-dione-1,2 (**9**) was isolated as the main product (0.20–0.36 mol) along with 0.35–0.42 mol of the starting quinone. When the reagents ratio was of 10 : 40 : 1, 0.36 mol of peroxide **9** and 0.38 mol of the quinone were found.

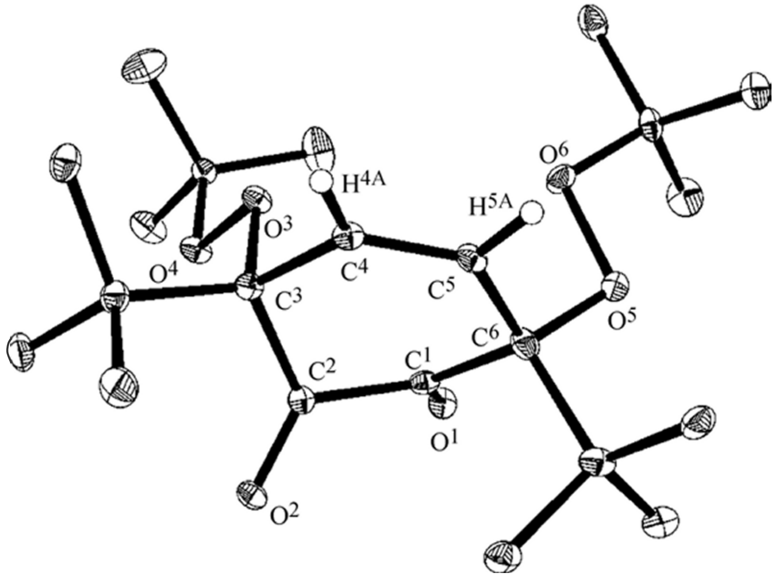
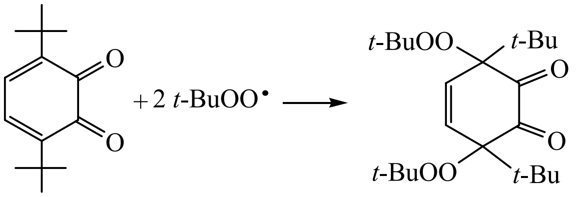


Fig. 1. Molecular structure of 3,6-di-*tert*-butyl-3,6-di-*tert*-butylperoxycyclohexene-4-dione-1,2 (**9**).

The molecular structure of diperoxide **9** was confirmed by X-ray diffraction method. The carbonyl groups were in the *trans*-configuration and the *tert*-butyl and *tert*-butyl peroxide groups were in the *cis*-configuration (Fig. 1). The values of the main bond lengths and bond angles in the *tert*-butylperoxy fragments were close to those of alkylperoxyanthracenes [14]. The experimental geometry parameters of the cyclohexene ring in **9** were as follows (distances are given in Å and angles are given in deg): C^1–C^2 and C^3–C^4 [1.504(4)], C^2–C^3 and C^1–C^6 [1.532(5)], C^5–C^6 [1.516(5)], C^4–C^5 [1.323(5)]; C^4–C^5–C^6, C^3–C^4–C^5 [124.8, 126.6(3)], C^2–C^3–C^4, C^1–C^6–C^5 [108.6, 106.8(3)], C^2–C^1–C^6 [113.4(3)], C^1–C^2–C^3 [116.4(3)].

The formation of peroxide **9** could be explained by the addition of *tert*-butylperoxy radicals to quinone **4** at the cycle conjugated bonds system [Eq. (11)].



(11)

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In order to verify the possibility of *tert*-butylperoxy radicals addition to quinone **4**, we performed its reaction with hydroperoxide **1** in the presence of di-*tert*-butylperoxalate (1 : 5 : 1, C_6H_6, 45°C, 6 h) and revealed the presence of 0.48 mol of diperoxide **9**, 0.01 mol of anhydride **8**, 0.07 mol of hydroxyquinone **5**, 0.11 mol of the starting quinone, 4.32 mol of *t*-BuOH, 0.01 mol of acetone, and 0.11 mol of *tert*-butyl peroxide in the mixture. Unlike the similar reactions with 9-*R*-anthracenes (in that case the *t*-BuOO˙ radicals are captured [14], and the chain process of *t*-BuOOH decomposition is suppressed [12]), the hydroperoxide was completely consumed in the reaction studied in this work. In the case of the **1**–**2** system, *tert*-butylperoxide radicals were formed both via decomposition of chromium trioxide [scheme (3)] and in the reaction of hydroperoxide **1** with *tert*-butoxy radicals formed on the stage of Cr^{4+} oxidation into chromyl.

According to the results reported in [15], benzoquinone **4** reacts with *t*-BuOOH (70°C) to form anhydride **8** and hydroxyquinone **5** as the major products. The authors have stated that the process occurs predominantly via the radical steps leading to the intermediate *o*-semiquinone and *tert*-butylperoxy radicals that are further transformed in the final products. In view of these data and our results we conclude that the reaction of quinone with hydroperoxide **1** was affected by chromium alkoxide, since formation of diperoxide **9** was not observed in [15].

In the reaction of quinone **4** with hydroperoxide **1** in the presence of $Co(acac)_2$ (1 : 5 : 1), up to 0.1 mol of epoxyquinone **6** was formed, and as the earlier unknown 4,4'-di-*tert*-butyl-2,2'-dipyvaloyl-[2,2'-bifuran]-5,5'(2*H*,2'*H*)-dione **10** (the major product) was isolated

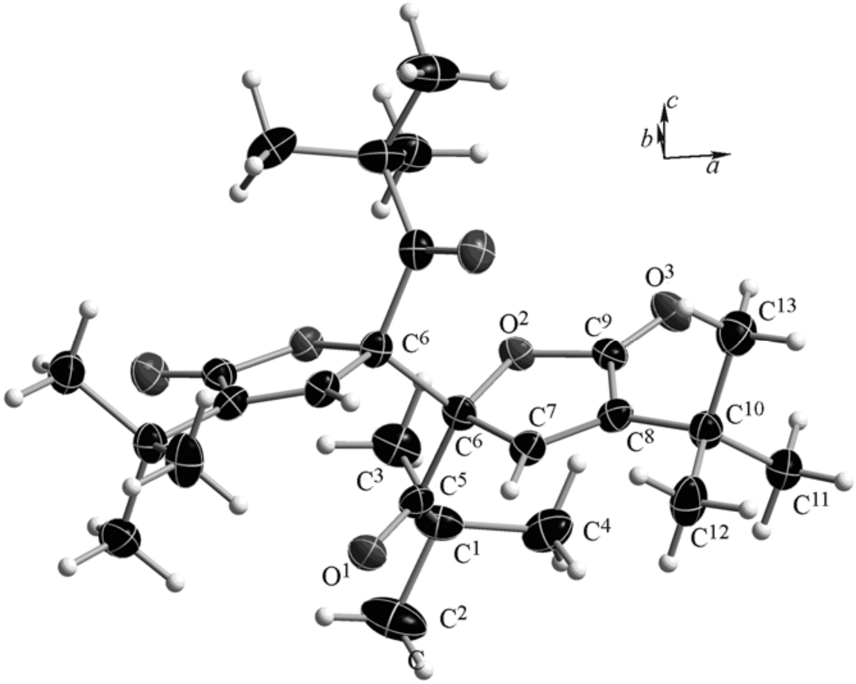


Fig. 2. Molecular structure of 4,4'-di-*tert*-butyl-2,2'-dipyvaloyl-[2,2'-bifuran]-5,5'(2*H*,2'*H*)-dione (**10**).

in the form of colorless crystals with the yield of 0.15–0.20 mol. Its structure was confirmed by X-ray diffraction analysis (Fig. 2) as well as ^{1}H and ^{13}C NMR spectroscopy. We believe that compound **10** was the product of the reaction of the initially formed pyrone intermediate with hydroperoxide or cobalt-containing peroxide [scheme (12)]. Traces of pyrone **7** were detected among the reaction products. The reaction of pyron **7** with hydroperoxide is shown below.

The hydroperoxide could be added at the carbonyl group of the pyrone to form oxyperoxide. Subsequent decomposition of the latter led either to cyclic dicarbonate (via insertion of oxygen into the C–C bond of the cycle) or to ketoperoxide (via insertion of oxygen at the C–O bond). Molecular or homolytic decomposition of peroxide might lead to 3-(*tert*-butyl)-5-pyvaloylfuran-2(5)*H*-one; interaction of the latter with the oxygen-containing radicals present in the cobalt alkoxide–*t*-BuOOH system at the tertiary C–H bond afforded the radicals that could dimerize to yield compound **10**.

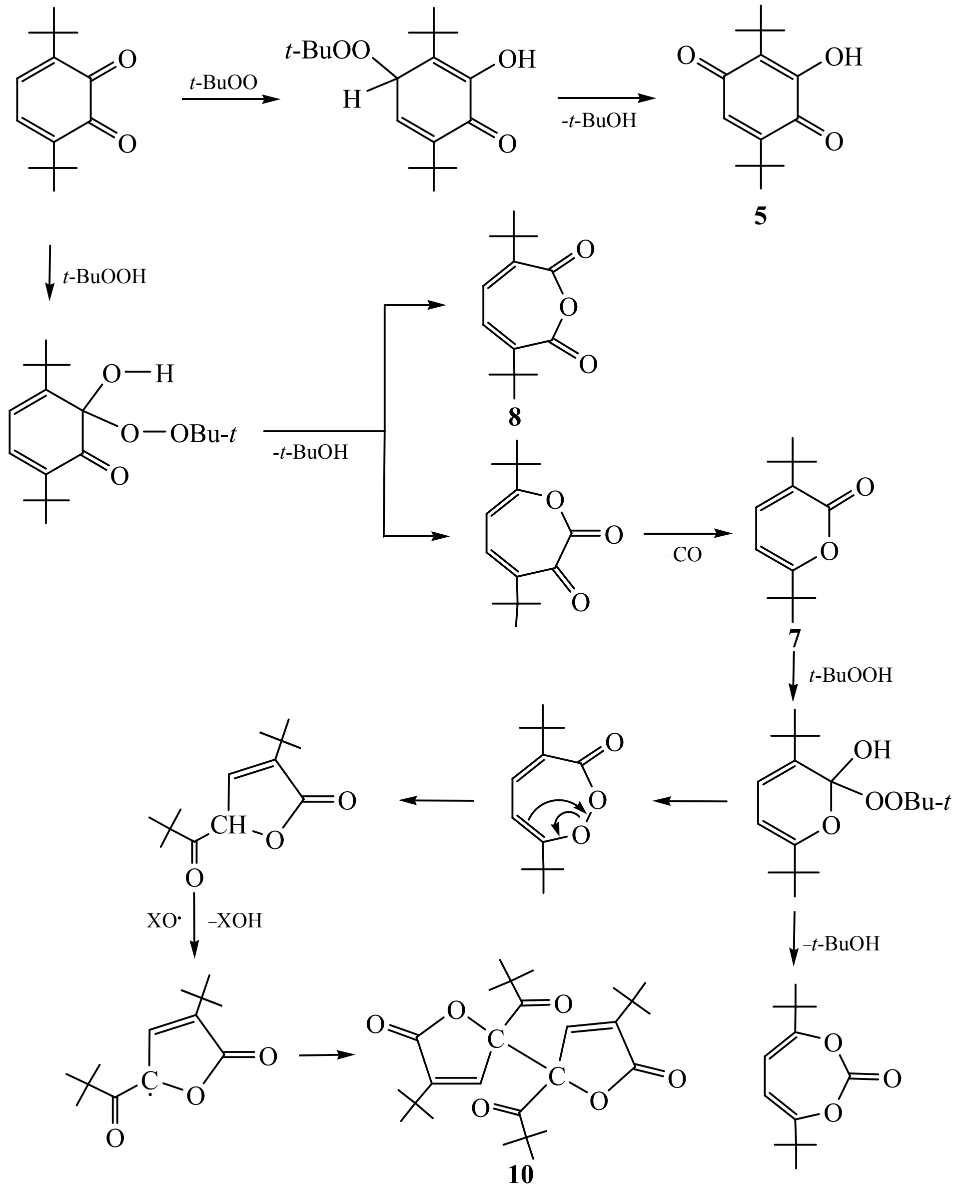
The reactions of the intra- and extradiol splitting of the *o*-qionine ring have been well studied using catalytic decomposition of 3,5-di-*tert*-butylcatechol and 3,5-di-*tert*-butyl-*o*-benzoquinone with oxygen [16, 17] or with hydrogen peroxide in an alkaline medium [18] as examples. The ring contraction reaction resulted in a set of products corresponding to the shift of the carbon atom from the ring to the side chain.

To summarize, the obtained results confirmed that the products of *o*-quinones oxidation with the hydroperoxide–metal alkoxide system were affected by the metal nature. That could be connected with the stability of the peroxy compound and polarity of the Me–OOBu-*t* bond. On top of that, the catalytic action of oxygen (its yield and the formation rate depending on the metal alkoxide nature) could not be excluded.

EXPERIMENTAL

Electronic absorption spectra were registered using a UV-1800 Shimadzu spectrophotometer. IR spectra were recorded using an IR Prestige-21 Shimadzu instrument (pellets with KBr or thin layer). NMR spectra of the solutions in $CDCl_3$ were recorded with an Agilent DD2 NMR 400 spectrometer at 400 (^{1}H) and 101 (^{13}C) MHz; the chemical shifts are reported in δ scale relative to Me_4Si.

X-Ray analysis of compound **9** was performed using a D8 Quest Photon diffractometer at 100 K



(12)

($\mathrm{Mo}K_{\alpha}$ radiation, graphite monochromator). The structure was solved via the direct method and refined by full-matrix least-square method over F^2 using SHELXL software package [19]. All non-hydrogen atoms were found from the differential Fourier electron density maps and refined anisotropically. Hydrogen atoms were placed in their geometrically calculated positions and refined using a *rider* model. Since the crystal of **9** was twin, the absorption was taken into account using TWINABS software [20]. Main crystallographic data and the unit cell parameters for compound **9** are as follows: $C_{22}H_{38}O_6$, $M = 398.52$, monoclinic crystal system, space group $P2_1$, $a = 6.404(4)$ Å, $b = 17.441(10)$ Å, $c = 10.516(6)$ Å, $\beta = 104.258(14)°$, $V = 1138.4(12)$ Å^3, $Z = 2$, $F(000) = 436$, $d_{\mathrm{calc}} = 1.163$ g/cm^3, $\mu = 0.083$ mm^{-1}, $\theta = 2.336°–24.586°$, 1985 independent reflections, GOF (F^2) = 1.069, $R_1 = 0.0486$, [$I > 2\sigma(I)$], $wR_2 = 0.0.1074$ (all data), $\rho_{\mathrm{max}}/\rho_{\mathrm{min}} = 0.436/–0.158$ e/Å^3.

Crystals of compound **10** obtained via slow evaporation of the ethyl acetate solution. The X-ray analysis was performed using an Oxford Xcalibur 3 automated diffractometer equipped with a Spellman generator (50 kV, 40 mA) and a Kappa CCD detector ($\mathrm{Mo}K_{\alpha}$, $\lambda = 0.71071$ Å). The structure was solved taking advantage of CrysAlis CCD [21], CrysAlis RED [22], SCALE3 ABSPACK [23], SHELXS-97

[24], SHELXL-97 [25], and PLATON [26] software. Main crystallographic data and the unit cell parameters for compound **10** are as follows: $C_{26}H_{38}O_6$, M = 446.56, orthorhombic crystal system, space group *Pbcn*, a = 13.4530(5) Å, b = 15.5263(6) Å, c = 12.3582(6) Å, V = 2581.32(19) Å^3, Z = 4, F(000) = 968, d_{calc} = 1.149 g/cm^3, μ = 0.080 mm^{-1}, θ = 4.22°–25.02°, 1639 independent reflections, GOF (F^2) = 1.033, R_1 = 0.0474, 0.1067 [$I > 2\sigma(I)$], wR_2 = 0.0733, 0.1219 (all data), ρ_{max}/ρ_{min} = 0.199/–0.165 e/Å^3. The structure of compound **10** was deposited at the Cambridge Crystallographic Data Centre, CCDC 1064054.

Chromatography analysis of the reaction products in liquid phase was performed using a GC-2010A (Shimadzu) instrument with flame ionization detector, using nitrogen as carrier gas, an Equity-5 capillary column (30000 × 0.32 mm), and the temperature programming mode from 50 to 170°C. The chromatograms were processed using the external reference method with authentic samples. The products were isolated via column chromatography on silica 60 (0.06–0.2 mm) using a petroleum ether–diethyl ether mixture or chloroform as eluent.

The carboxylic acids were identified qualitatively and quantitatively after transformation in the methyl esters via the treatment with diazomethane. The carbonyl compounds were identified in the form of 2,4-dinitrophenylhydrazones by measuring the melting point and by TLC [comparing the R_f values of the sample and the reference compounds; Silufol UV-254, tetrachloromethane–diethyl ether or benzene–diethyl ether (9 : 1) as eluent]. Chromium content was determined using the Palmer method [27].

Tetra-*tert*-butoxychromium was synthesized via the known procedure [28]. Found Cr, %: 15.07. $C_{16}H_{36}O_4Cr$. Calculated Cr, %: 15.09. Trimethylsilylmethanol was obtained via alcoholysis of trimethylsilylmethyl acetate, bp = 121–122°C, n_D^{20} = 1.4070 [29]. 1,2-Diphenylethanol was recrystallized from the 1 : 1 benzene–petroleum ether mixture, mp = 63°C [30]; *D,L*-borneol was recrystallized from petroleum ether, mp = 209–210°C [24]. 1,1,2-Triphenylethane-1,2-diol was synthesized from ethyl mandelate and bromobenzene, mp 126°C [31]. Benzopinacol was prepared via the reduction of benzophenone, mp 185–186°C (decomp.) [32]; *trans*-1,1'-dioxydicyclohexyl was prepared via the reduction of cyclohexanone, mp = 122°C [33]. 3,6-Di-*tert*-butylcatechol was recrystallized from ethanol, mp 83–84°C [34]. Commercial neopentyl alcohol (99%) and methyl-(*S*)-lactate (98%) (Aldrich) were used as received. Concentration of the major component in *tert*-butylhydroperoxide was of 99.5–99.6%.

Oxidation of the primary and secondary alcohols was performed via successive addition of the alcohol and hydroperoxide **1** to the benzene solution. The reaction mixtures were incubated at room temperature during one day. The solvent and the volatile products were distilled off and condensed in a trap cooled by liquid nitrogen for further GC analysis. In certain cases, the residue was hydrolyzed with 10% H_2SO_4 after removal of the volatile compounds; the products were extracted with ether; the extract was dried with sodium sulfate and analyzed. The main product of oxidation of 1,2-diphenylethanol was phenyl benzyl ketone (isolated in the pure state; mp 56°C; the ^{1}H and ^{13}C NMR spectra were identical to those of the reference sample).

Oxidation of trimethylsilylmethanol with the *t*-BuOOH–Cr(OBu-*t*)$_4$ system (10 : 30 : 1). 0.094 g of Me_3SiCH_2OH and 0.24 g of the hydroperoxide were successively added to the solution of 0.031 g of alkoxide **2** in 10 mL of benzene. The reaction occurred exothermally, the mixture color changing from bright blue to red-brown. The solution turned colorless and transparent after 20 h, and a small amount of brown gel-like precipitate was found at the bottom. Filter paper soaked with $PdCl_2$ solution and placed over the reaction mixture immediately turned black due to formation of the metal carbonyl $[(CO)PdCl_2]_2$. 0.13 g of *t*-BuOH, 0.0036 g of (*t*-BuO)$_2$, 0.10 g of *t*-BuOOH, 0.01 g of $Me_3SiOOBu$-*t*, 0.038 g of $Me_3SiOCH_2SiMe_3$, 0.014 g of Me_6Si_2O, and 0.039 g of Me_3SiOH were found in the condensed volatile fraction.

For additional identification of trimethylhydroxysilane, several drops of 10% H_2SO_4 were added to the aliquot of the reaction solution, the mixture was stirred and incubated during 12 h. The organic phase was separated off, washed with water, dried over sodium sulfate, and analyzed by GC. The peak of Me_3SiOH disappeared, the mass of hexamethylsiloxane was 0.05 g. Hence, treatment with the acid gave additionally 0.036 g of hexamethylsiloxane corresponding to 0.039 g of Me_3SiOH.

Reaction of methyl lactate with the *t*-BuOOH–Cr(OBu-*t*)$_4$ system (1 : 3 : 1). 0.08 g of methyl lactate and 0.21 g of *t*-BuOOH were added to 0.27 g of Cr(OBu-*t*)$_4$ in 10 mL of benzene; the mixture color turned from blue to red-brown and then to yellow-brown. The color did not change after 20 h incubation, and fine brown precipitate was formed at the bottom. 0.35 g of *t*-BuOH, 2.3 mg of $(t\text{-BuO})_2$, 3.5 mg of acetone, 0.06 g of methyl pyruvate, and 0.018 g of the starting ester were found in the condensate of the solvent and volatile fractions. The dry residue was hydrolyzed with 10% H_2SO_4, extracted with ether, dried over Na_2SO_4, and analyzed. 1.5 mg of MeC(O)COOMe and 2.1 mg of MeCH(OH)COOMe were found.

For chemical identification of the carbonyl compounds, condensates from several experiments were combined, and the first portion (about one tenth of the total volume) was distilled to a solution of 2,4-dinitrophenylhydrazine (2,4-DNPH). The formed 2,4-dinitrophenylhydrazone of acetone was identified by TLC (eluent: 9 : 1 C_6H_6/Et_2O). Treatment of the rest of the solution with 2,4-DNPH gave bright-yellow precipitate. 2,4-Dinitrophenylhydrazones of two isomers of methyl pyruvate were isolated by column chromatography (chloroform): (1) mp 158°C and (2) mp 195°C. IR spectrum (KBr), ν, cm^{-1}: (1) 3313 (N–H), 1718 (C=O) and (2) 3383 (N–H), 1700 (C=O). UV spectrum (EtOH), λ, nm: (1) 350 and (2) 361.

Reaction of 1,1'-dioxydicyclohexyl with $Cr(OBu\text{-}t)_4$. 0.13 g of the diol was added to 0.22 g of the chromium alkoxide in 10 mL of benzene. The dark-blue solution turned green after 20 h (20°C). Benzene and volatile products were distilled off and condensed in the trap cooled with liquid nitrogen; brown precipitate was formed in the condensate. The condensate analysis revealed the presence of 0.089 g of *t*-BuOH and 1.5 mg of chromium, corresponding to 0.01 g of $Cr(OBu\text{-}t)_4$. The residue after removal of the volatile products was dry dark-green precipitate. Found Cr, %: 12.98. $C_{20}H_{38}CrO_4$. Calculated Cr, %: 13.20.

Oxidation of 1,1'-dioxydicyclohexyl with the *t*-BuOOH–$Cr(OBu\text{-}t)_4$ system (1 : 3 : 1, 20°C). 0.123 g of pinacol and 0.19 g of the hydroperoxide were added to a solution of 0.21 g of the alkoxide in 10 mL of benzene. The color of the solution turned from dark-blue to wine-red and then to brown. After 20 h incubation, the volatile products were isolated as described above. 0.28 g of *t*-BuOH, 0.01 g of $(t\text{-BuO})_2$, 1 mg of acetone, and 0.078 g of cyclohexanone were detected in the bright-yellow condensate. Part of the solution was treated with 2,4-DNPH, and the ketone derivative was isolated, its mp (160°C) coinciding with that of 2,4-dinitrophenylhydrazone of cyclohexanone, PPh_3, was added to the rest of the condensate. The mixture turned colorless within several minutes, and flake-like precipitate was formed, indicative of the presence of chromium compounds in the form of Cr^{+5}=O in the condensate [35]. The dry residue was mixed with benzene, and the insoluble chromium compounds were filtered off. The solvent was removed under reduced pressure to give 0.019 mg of the starting pinacol.

The reactions of other α-diols given in Table 2 and the products analyses were performed similarly. Benzophenone was identified in the form of the derivative with 2,4-dinitrophenylhydrazine. In order to determine the amount of the unreacted pinacol, the liquid phase of the reaction mixture was separated from chromium compounds, and benzophenone was washed with alcohol. The unreacted benzopinacol remained at the filter, mp 186ºC.

Reaction of 3,6-di-*tert*-butyl-*o*-benzoquinone with the *t*-BuOOH–$Cr(OBu\text{-t})_4$ system (1 : 5 : 1, 20°C). 0.25 g of quinone and 0.52 g of the hydroperoxide (portionwise) were added to the solution of 0.30 g of $Cr(OBu\text{-}t)_4$ in 30 mL of benzene; the mixture was slightly heated spontaneously. During the first 5 min of the reaction gas was evolving (apparently, it was oxygen, since CO was detected in the gas phase only after 30–60 min). The blue-green solution turned red-brown. 8 mg of hydroxyquinone **5**, 0.01 g of anhydride **8**, and 0.094 g of the starting quinone **4** were detected in the mixture by chromatography after one day of the reaction. After 30 h incubation, the solvent and the volatile products were isolated as described above. 6 mg of acetone, 6.6 mg of methyl *tert*-butyl ether, 0.02 g of *tert*-butylperoxide, and 0.55 g of *t*-BuOH were detected in the condensate. *tert*-Butyl hydroperoxide was absent. The intense yellow color of the condensate disappeared after treatment with triphenylphosphine, suggesting the presence of $(t\text{-BuO})_3CrO$ [4].

The residue was analyzed by column chromatography (eluent: petroleum ether–Et_2O, 22 : 1 and then 22 : 5). Two main fractions were obtained. The first fraction (0.165 g) was 3,6-di-*tert*-butyl-3,6-di-*tert*-butylperoxycyclohexene-4-dione-1,2, light-yellow crystalline compound, mp 135–137°C (decomp.). IR spectrum (KBr), ν, cm^{-1}: 3082, 3067, 2985, 2975, 2931, 2875, 1738 (CO), 1474, 1465, 1388, 1367, 1200, 1127, 971, 901, 879, 686. ^1H NMR spectrum, δ, ppm: 1.07 s [9H, $C(CH_3)_3$], 1.19 s [9H, $C(CH_3)_3$], 6.28 s [1H, CH=]. ^{13}C NMR spectrum, δ_C, ppm: 26.31 [$C(\underline{C}H_3)_3$], 26.60 [OC($\underline{C}$H$_3$)$_3$], 39.57 [$\underline{C}$(CH$_3$)$_3$], 81.20 [O$\underline{C}$(CH$_3$)$_3$], 89.02 [$\underline{C}$–OOBu-*t*], 133.05 [H$\underline{C}$=], 198.19 [C=O]. The second fraction (0.116 g) contained the unreacted quinone. After washing it with isooctane, 0.098 g of 3,6-di-*tert*-butyl-*o*-benzoquinone was obtained, mp 208–209°C.

Reaction of 3,6-di-*tert*-butyl-*o*-benzoquinone with *tert*-butylhydroperoxide in the presence of cobalt acetylacetonate (1 : 5:1, C_6H_6, 20°C). 0.20 g of quinone **4** and 0.41 g of the hydroperoxide **1** were added to a solution of 0.233 g of the cobalt alkoxide in 18 mL of benzene. The green reaction mixture turned dark-brown after several minutes, and finally moss green solution was formed with brown precipitate at the bottom after 20 h. Carbon oxide CO was detected in the flask over the solution. 2 days later the solvent and volatile products were condensed in a trap cooled with liquid nitrogen. 0.28 g of *t*-BuOH was detected in the solution, the starting hydroperoxide was absent.

The residue, dark-green mass, crystallized upon incubation and was then purified of the metal via column chromatography (petroleum ether : diethyl ether = 22 : 1). The eluate was concentrated and analyzed by chromatography. The starting benzoquinone was absent, and traces of hydroxyquinone **5**, pyrone **7**, and anhydride **8** were found. After removal of the solvent, 3 mL of petroleum ether was added to the residue, and the dissolved part was decanted. The remained colorless crystals were washed with 1 mL of petroleum ether to give 0.089 g of crystalline compound **10**, mp 189°C. IR spectrum (KBr), ν, cm^{-1}: 2975, 2965, 2934, 2873, 1777, 1775, 1702, 1694, 1481, 1462, 1396, 1318, 1260, 1131, 1097, 1032, 1004, 985, 934, 887. ^{1}H NMR spectrum, δ, ppm: 1.16, 1.25, [18H, C(CH$_3$)$_3$], 6.90 (1H, CH=). ^{13}C NMR spectrum, δ_C, ppm: 27.96 [($\underline{C}$H$_3$)$_3$C–CO], 29.16 [($\underline{C}$H$_3$)$_3$C], 32.05 [$\underline{C}$(CH$_3$)$_3$], 46.30 [(CH$_3$)$_3$C–CO], 94.77 [C$_3\underline{C}$–O], 144.54, 144.59 [H$\underline{C}$=$\underline{C}$]. 170.19 [C=O, furan], 206.01 [C=O, ketone].

According to the IR spectroscopy data, the oily residue contained compound **10** along with non-identified carbonyl-containing compounds (ν, cm^{-1}: 1723, 1740).

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