Reactions of Titanium Alcoholates Ti(OR)_4 (R = *n***-Bu,** *t***-Bu) with Tertiary Organic and Organometallic Hydroperoxides**

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Abstract — *tert*-Butyl and cumyl hydroperoxides in the reactions with $Ti(OR)_4$ are reduced to alcohols with the evolution of oxygen via formation of titanium-containing peroxides and trioxides. The pathways of the reactions of $Ti(OR)_4$ with triphenylelement hydroperoxides R_3EOOH (E = C, Si, Ge) depend on element E and on the structure of R; the reactions involve the rearrangement of the peroxides, and with (*n*-BuO)₄Ti the alkoxy group is oxidized either with preservation or with breakdown of the hydrocarbon skeleton. **DOI:** 10.1134/S1070363206020137

Titanium alcoholates are used as catalysts of hydroperoxide oxidation of oxygen-containing organic substrates. The compounds $Ti(OR)_4$ (R = Et, *i*-Pr, *t*-Bu) are used in stereoselective epoxidation of allyl alcohols (Sharpless epoxidation) [1–3]. The epoxidizing system is an equimolar mixture of Ti(OR)₄, tertiary hydroperoxide, and dialkyl tartrates (alkyl = ethyl, isopropyl). The dimer $[Ti(tartrate)_2(OR)]_2$ is an active catalyst. tert-Butyl hydroperoxide I in the presence of titanium tetraisopropylate (3:1) under mild conditions (CH₂Cl₂, -23 to 20°C) oxidizes substituted phenols, and also naphthols, phenanthrols, and anthracenols, to the corresponding *o*-quinones [4]. Primary and secondary benzyl alcohols are selectively converted to the corresponding aldehydes or ketones in high yields under the action of **I** and catalytic amounts (0.1 mol) of Ti(OPr-i)₄ [5]. Aliphatic hydroxy groups, double bonds (except allyl bonds relative to the OH group), and phenolic hydroxyls (except those located in the *o*-position of the benzene ring) remain intact. All these reactions involve fast ligand exchange of the titanium alkoxy groups with allyl and benzyl alcohols, phenols, and hydroperoxides. The oxygen-containing substrates are oxidized by the intramolecular mechanism, without generation of free radicals.

Titanium alcoholates in combination with various oxidants (singlet oxygen, ROOH) were suggested as reagents for one-step synthesis of epoxidized alcohols from alkenes [6]. The reactions involve formation of hydroperoxides and their subsequent transformation in the presence of titanium alcoholates into epoxy alcohols via unsaturated alcohols. A scheme of intermolecular epoxidation was suggested.

Despite the fact that all the above processes involve titanium-containing peroxides, data on reactions of titanium alcoholates with hydroperoxides are few. It was reported that the reaction of $Ti(OPr-i)_4$ with hydroperoxide **I** yielded titanium peroxy compounds, which were not isolated pure [7], and that the isopropoxy group can be oxidized with **I** to acetone [5]. The possibility of the oxidation of the alkoxy group in $(n-BuO)_4Ti$ with **I** was demonstrated in [8].

The major pathway in the reaction of tetra-*tert*butoxytitanium with hydroperoxide **I** in a 1 : 2 ratio is the release of oxygen (yield 0.85-0.90 mol) [9–11] via formation of titanium-containing peroxide and trioxide. The trioxide decomposes along two pathways: release of oxygen and regeneration of titanium alcoholate [9] and homolysis of the peroxide bonds [10].

In this study we examined the reactions of titanium alcoholates with hydroperoxides with the aim to elucidate how the reaction pathways are influenced by the structures of alkoxy groups in titanium alcoholates and of hydroperoxides, and also by the kind of the atom bonded to the hydroperoxy group.

Among titanium alcoholates we chose titanium tetrabutylate II and tetra-*tert*-butylate III. In the former compound, alkoxy groups contain α -H atoms and thus are capable of oxidation. We chose tertiary hydroperoxides containing methyl and phenyl groups: *tert*butyl hydroperoxide I, cumyl hydroperoxide IV, 1,1diphenylethyl hydroperoxide V, triphenylmethyl hydroperoxide VI, and heteroanalogs of VI: triphenylsilyl hydroperoxide VII and triphenylgermyl hydroperoxide VIII. All the reactions were performed in benzene at room temperature. The alcoholate : hydroperoxide ratio was 1 : 2 for methyl(phenyl) hydroperoxides and 1 : 1 for triphenylelement hydroperoxides VI-VIII.

Reaction products	R						
	Me ₂ (Ph)C ^b	Ph ₂ (Me)C ^b	Ph ₃ C ^c	Ph ₃ Si ^c	Ph ₃ Ge ^c		
		Volatile product	ts		1		
0,	0.65	0.05	-	0.13	0.31		
t-BuOH	2.86	2.54	1.69	1.58	0.90		
PhCOMe	0.04	0.15	_	_	_		
	Products	of hydrolysis of non	volatile residue ^d		•		
t-BuOH	0.70	0.88	1.82	2.29	0.96		
PhCOMe	0.05	0.14	_	_	_		
ROH	1.80 ^e	0.91 ^f	0.42	0.70	0.10 ^g		
Alkene	0.03	0.29	_	_	_		
	[PhC(Me)=CH ₂]	$(Ph_2C=CH_2)$					
PhOH		0.10	0.13	0.15	0.04		
			(traces)				
Ph ₂ EO	-	0.03	0.32	0.25 ^h	_		
R'ÕOOH	0.06 ⁱ	j	j	0.04 ⁱ	0.07^{i}		
			1	1	1		

Table 1. Products of reactions of titanium tetra-*tert*-butylate $(t-BuO)_4$ Ti with hydroperoxides RCOOH (yield, mole per mole of titanium alcoholate; benzene, 20° C)^a

⁴ Averaged results. ^b $(t-BuO)_4Ti:ROOH = 1:2$. ^c $(t-BuO)_4Ti:ROOH = 1:1$. ^d Metal ~1 mol in all the experiments; with Ph₃GeOOH, the volatile fraction contained 0.47 mol of Ti(OBu-*t*)₄. ^e The volatile fraction contained 0.25 mol of alcohol. ^f 0.27–0.25 mol of Ph₂C(Me)OOH remains unchanged. ^g We also isolated Ph₆Ge₂O: 0.39 mol before hydrolysis and 0.04 mol in the hydrolysis products. ^h In the form of diphenylsiloxane. ⁱ Acetic : formic acids ~1:5. ^j Not determined.

The results of the reactions of titanium alcoholates with hydroperoxides are given in Tables 1 and 2. In all the cases, irrespective of the structure of the alkoxy group bonded to Ti, the reactions with methyl(phenyl) hydroperoxides involve the release of oxygen and reduction of the hydroperoxides to the corresponding alcohols. Scheme (1) illustrating the reaction pathway is similar to that suggested previously for the reactions of aluminum *tert*-butylate and alcoholate **III** with hydroperoxide **I** [10–12].

$$(RO)_{4}Ti + R'OOH \xrightarrow{-ROH} (RO)_{3}TiOOR' \xrightarrow{A}$$

$$\xrightarrow{R'OOH} \begin{bmatrix} R'-O-O-H \\ \downarrow & \downarrow \\ (RO)_{3}Ti-O-O-R' \end{bmatrix} \longrightarrow R'OH + \begin{bmatrix} R'-O^{3}-O^{2} \\ \downarrow & \downarrow \\ (RO)_{3}Ti-O^{1} \end{bmatrix} \longrightarrow O_{2} + (RO)_{3}TiOR', \quad (1)$$

$$\xrightarrow{B}$$

R = t-Bu, *n*-Bu; R' = t-Bu, PhCMe₂, Ph₂CMe.

Scheme (1) involves formation of intermediate titanium-containing peroxides **A**, as indicated by a high yield of alcohols ROH in the volatile fraction and of trioxides **B**. These compounds mostly decompose to unsymmetrical titanium alkoxides and molecular oxygen (partially singlet). In the reactions of hydroperoxide **I** with alcoholates **II** and **III**, we detected formation of 0.35-0.40 mol of singlet oxygen (by its reaction with anthracene). The yield of oxygen depends on the structure of substituents in titanium alcoholates and hydroperoxides. In the reaction of **IV** with alcoholate **III** it is almost 1.5 times higher than in the reaction with **II**. In the reactions of **III** with methyl(phenyl) hydroperoxides, with an increase in the number of phenyl groups, the yield of oxygen decreases, but in the reaction with **VIII** it reaches 0.30-0.32 mol (60-64%) (Table 1). No oxygen formation was detected in the reactions of **II** with triphenylelement hydroperoxides **VI–VIII**.

Reaction products	R								
	<i>t</i> -Bu ^b	Me ₂ (Ph)C ^b	Ph ₃ C ^c	Ph ₃ Si ^c	Ph ₃ Ge ^c				
Volatile products ^d									
O ₂	0.34	0.40	_	_	-				
PrCHO	0.20 ^e	0.46	0.26	0.30	0.35^{t}				
CH ₃ CH=CH ₂	_	_	0.01	0.58	0.51				
BuŎH	1.67	2.14	1.25	1.44	1.86				
ROH	1.36	0.54 ^g	-	_	_				
Products of hydrolysis of nonvolatile residue									
PrCHO	0.17	0.16	0.20	Traces	0.12				
BuOH	1.40	0.71	1.69	1.49	0.89				
PhOH	_	_	0.30	0.10	_				
Ph ₂ EO	-	-	0.41						
RÕH	0.29	1.22	0.42 ^h	0.20^{1}	0.16 ¹				
(Ph ₃ EO) ₄ Ti	-	-	-	0.18^{k}	0.16 ^K				
PrCOOH	0.20	0.14	0.10	0.05	0.10				
НСООН	_	0.015	0.015	Traces	0.02				

Table 2. Products of reactions of titanium tetrabutylate $(n-BuO)_4$ Ti with hydroperoxides RCOOH (yield, mole per mole of titanium alcoholate; benzene, 20° C)^a

^a Averaged results. ^b (*n*-BuO)₄Ti : ROOH = 1 : 2. ^c (*n*-BuO)₄Ti : ROOH = 1 : 1. ^d Formaldehyde was identified qualitatively in all the cases. ^e 0.04 mol of butyl butyrate was also detected. ^f Reaction time 10 h at 20°C and 3 h at 60°C. ^g 0.11 mol of acetophenone was also detected in the volatile fraction and hydrolysis products. ^h 0.05 mol of triphenylmethyl peroxide was also detected. ⁱ A mixture of triphenylhydroxysilane and diphenylsiloxane. ^j Ph₆Ge₂O. ^k Compounds (Ph₃EO)₄Ti (E = Si, Ge) were isolated before hydrolysis.

The decomposition of trioxides **B** occurs concurrently with their homolysis across the O^2-O^3 bond [10–12]. An ESR monitoring of the reactions of titanium alcoholates with hydroperoxides **I**, **IV**, and **V** in benzene at 20°C in the absence of spin traps revealed a singlet (g_i 2.0125–2.013) which was assigned to the peroxy radical (RO)₃TiOO [10–12], since the *t*-BuOO radical is not detected under these conditions.

An ESR monitoring of the reaction of $(n-\text{BuO})_4\text{Ti}$ with Ph₃COOH also revealed a signal characteristic of the peroxytitanium radical (g_i 2.013), which suggests formation of trioxide **B** (R = Bu, R' = CPh₃). Homolysis of trioxide **B** across the O¹–O² bond followed by recombination of the Ph₃COO' radicals accounts for the formation of triphenylmethyl peroxide [yield 0.05 mol; scheme (2)].

$$(BuO)_3TiOOOCPh_3 \longrightarrow (BuO)_3TiO + OOCPh_3,$$

 $2Ph_3COO \longrightarrow Ph_3COOCPh_3 + O_2.$ (2)

As follows from Tables 1 and 2, the reactions of titanium alcoholates with hydroperoxides are not limited to formation and transformations of trioxides **B**. The qualitative and quantitative composition of products formed in the reactions of $(n-BuO)_4Ti$ and $(t-BuO)_4Ti$ with hydroperoxides, especially with tri-

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phenylelement hydroperoxides, is also determined by transformations of titanium peroxy compounds **A**. The formation of titanium peroxy derivatives $(RO)_3Ti$. OOR' from hydroperoxides Ph₃EOOH is favored by the proton-donor power of these hydroperoxides, decreasing in the order Ph₃SiOOH > Ph₃GeOOH > Ph₃COOH, in accordance with extent of $d\pi$ -p π conjugation [13]. Therefore, the reactions of titanium alcoholates with these hydroperoxides were performed at a reactant ratio of 1 : 1.

The titanium-containing peroxides $(BuO)_3 TiOOR'$ decompose along several pathways. The common reaction for butoxytitanium and all the hydroperoxides is the oxidation of the alkoxy group (with the preservation of its carbon backbone) to butanal (Table 2). The aldehyde is formed by intramolecular decomposition [reaction (3)] of peroxide **A** in the six-membered reaction complex [5–8]:

$$(BuO)_{2}Ti \xrightarrow{O} CHPr \\ O \xrightarrow{I} H \xrightarrow{O} PrCHO + R'OH + [(BuO)_{2}TiO]_{x},$$
(3)
$$\stackrel{|}{R'} R' = t-Bu, PhCMe_{2}, Ph_{3}E (E = C, Si, Ge).$$

Butanal partially condenses into an ester, is oxidized to the acid, and reacts with titanium alcoholate in the enol form [14]; owing to the latter reaction, up to 0.17 mol of the aldehyde was detected in the hydrolysis products.

Along with butanal, in the volatile fraction from all the reactions with **II** we identified formaldehyde, and in the case of hydroperoxides **VII** and **VIII** we detected significant amounts of propene. Formaldehyde and propene are formed by destructive oxidation of the alkoxy group. We believe that this reaction occurs as decomposition [reaction (4)] of peroxides $(BuO)_3Ti$. OOR' in the eight-membered intermediate reaction complex.

 $\longrightarrow \text{R'OH} + \text{CH}_2\text{O} + \text{CH}_3\text{CH} = \text{CH}_2 + [(\text{BuO})_2\text{TiO}]_x, (4)$ $\text{R'} = \text{Ph}_3\text{C}, \text{Ph}_3\text{Si}, \text{Ph}_3\text{Ge}.$

The destructive oxidation is the most characteristic of organometallic hydroperoxides (E = Si, Ge), which may be due to steric factors. In going from C to Si and Ge, the covalent radius of the element appreciably increases (0.077, 0.117, and 0.122 nm, respectively [15]), as does also the volume of the Ph₃E group, which makes the formation of the eight-membered ring more preferable.

Propene was determined quantitatively in the form of isopropyl chloride after the treatment with HCl. Formaldehyde was identified in the form of its dimedone derivative and 2,4-dinitrophenylhydrazone, and also in the form of formic acid, which, in turn, was identified as methyl ester in the hydrolysis products. We failed to determine H₂CO quantitatively, because of its strong tendency to enter condensations. The IR spectra of hydrolysis products of the nonvolatile residues after the removal of volatiles contain a number of bands at 1020–1080 cm⁻¹ assignable to the stretching vibrations of the C–O–C groups.

The third pathway [reaction (5)] involving the loss of the peroxide oxygen consists in the rearrangement of titanium-containing peroxides and decomposition of the forming titanium alkoxy compounds C, similarly to aluminum peroxy compounds [16].

$$(BuO)_3 TiOOEPh_3 \longrightarrow (BuO)_3 TiOEPh_2(OPh)$$

 C
 $\longrightarrow Ph_2 EO + (BuO)_3 TiOPh.$ (5)

Rearrangement (5) makes the largest contribution in the case of the reaction of **II** with **VI**, which is caused by the formation of benzophenone. This transformation occurs to a lesser extent in the reactions with **VII** and was not detected in the reaction with Ph_3GeOOH .

It should be noted that the rates of the reactions of $(BuO)_4Ti$ with Ph_3EOOH strongly depend on element E. In particular, the reaction with Ph_3SiOOH is complete in 10–15 min, that with Ph_3COOH , in 30 min, and in the reactions with Ph_3GeOOH even after 3 h about 50% of the hydroperoxide remains unchanged. However, even under these conditions the amount of BuOH in the volatile fraction is equal to, or exceeds 1 mol. This fact suggests that the peroxide (BuO)_3TiOOGePh_3 (A) is formed fairly rapidly but decomposes slowly.

Thus, the reaction of $(BuO)_4Ti$ with tertiary hydroperoxides depends on the structure of their substituents and on the kind of the element bonded to the hydroperoxy group. Methyl(phenyl) hydroperoxides react with the release of oxygen. All the hydroperoxides ROOH oxidize the alkoxy group to butanal, and in the case of the Ph₃Si and Ph₃Ge derivatives this group undergoes destructive oxidation with the formation of formaldehyde and propene.

The reaction of (t-BuO)₄Ti with hydroperoxides V and VI occurs within 10–20 h, and ~30 min is sufficient for the completion of the reactions with triphenylelement hydroperoxides. With titanium tetra*tert*-butylate, reactions (3) and (4) are impossible. However, transformations of the *tert*-butoxy group do occur, as indicated by the presence of carboxylic acids (HCOOH, CH₃COOH) in the products of hydrolysis of the nonvolatile residues (Table 1). Also, in the volatile fraction of products from the reaction of III with VIII, we qualitatively detected isobutylene oxide, which may be formed by the decomposition [reaction (6)] of the titanium peroxy compound involving the β -H atom of the alkoxy group.

$$(t-BuO)_{2}Ti \bigvee_{\substack{O-O-GePh_{3}\\H}\\O-C-CH_{2}\\Me Me} \longrightarrow Me_{2}C-CH_{2} + Ph_{3}GeOH + [(t-BuO)_{2}TiO]_{r}.$$
 (6)

In contrast to the reactions of $(BuO)_4$ Ti, transformations involving the *tert*-butoxy group do not prevail. Along with the release of oxygen [scheme (1)], a significant contribution is made by rearrangement (5) of titanium peroxy compounds **A**. This process is the

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most characteristic of hydroperoxides **V**–**VII**. The yield of acetophenone and benzophenone reaches 0.30-0.32 mol. The IR spectrum proves the presence of benzophenone [v(C=O) 1680 cm⁻¹] in the nonvolatile fraction of the reaction products before hydrolysis. Also, the spectrum contains a band at 1265 cm⁻¹ assigned to the C–O stretching vibrations in the phenoxy group [comparison with the spectrum of an authentic sample of (*t*-BuO)₃TiOPh]. The similar band is also present in the spectrum of the nonvolatile residue from the reaction of **III** with Ph₃SiOOH. Diphenylsiloxane was isolated after hydrolysis of compound **C**.

The stoichiometry of rearrangement (5) suggests formation of equimolar amounts of Ph₂EO and phenoxytitanium. However, actually the yield of phenol was always considerably lower, and in some cases it was not detected at all. We assumed further oxidation of the phenoxy group. To check this assumption, we performed oxidation of phenol with the system alcoholate III-t-BuOOH in a 1:1:2 ratio in benzene and the reaction of specially synthesized (t-BuO)₃TiOPh with hydroperoxide I (1 : 1). The reaction mixtures become dark brown, as in the reactions of III with V-VII. From the volatile fraction, we isolated 4.2-4.5 and 1.7 mol of t-BuOH, respectively, and from the hydrolysis products of the nonvolatile residue, 0.40-0.45 mol of unchanged phenol in both cases. Hence, more than 0.50 mol of phenoxy groups react with the oxidants.

To identify transformation products of the phenoxy groups, the systems (t-BuO)₄Ti-PhOH-t-BuOOH and (t-BuO)₄Ti-Ph₃SiOOH were studied by ESR and IR spectroscopy. The ESR spectra of reaction mixtures from reactions of phenol with the system III-I, recorded in the presence of a spin trap (2-methyl-2-nitrosopropane), contained no signals from adducts of alkoxy or phenoxy radicals. Hence, the peroxide bond does not undergo homolysis. We detected a weak unidentified signal of a complex structure, which was apparently a superposition of signals from spin adducts of several carbon-centered radicals. The IR spectra of the hydrolysis products after steam distillation of phenol (dark brown viscous mass) contained bands at 1055-1280 cm⁻¹ characteristic of stretching vibrations of the Ph-OH and C=C-O-C groups and a broad band of OH stretching vibrations (3400 cm⁻¹). We have not isolated pure any products of phenol oxidation.

Thus, the reaction of (t-BuO)₄Ti with hydroperoxides **V**–**VII** involves formation of the corresponding titanium-containing peroxides, which undergo a rearrangement, and decomposition of the alkoxy derivatives $(t-BuO)_3 TiOE(R)(Ph)OPh$ to Ph(R)EO and phenoxytitanium (E = C, R = Me, Ph; E = Si, R = Ph). The phenoxy group in phenoxytitanium undergoes further oxidation with the formation of a complex mixture of products.

In the reaction of **III** with **VIII**, the contribution of the rearrangement of (t-BuO)₃TiOOGePh₃ is low; the amount of phenol is 0.04-0.05 mol. Ph₃GeOOH is reduced to the hydroxygermane transforming under the reaction conditions into hexaphenylgermanoxane. In contrast to the reactions with VI and VII, the volatile fraction contained up to 0.50 mol of the starting titanium alcoholate and 0.8-0.9 mol of t-BuOH, which is almost two times lower than in the similar reactions with VI and VII (Table 1). Table 1 shows that one of the major products of the reaction of (t-BuO)₄Ti with Ph₃GeOOH is oxygen. In specially performed reactions of **III** with **VIII** in a 1 : 2 ratio, the oxygen yield was 0.60-0.64 mol. An anthracene test showed that oxygen was released in the singlet form; 0.05 mol of anthraquinone was obtained.

The formation of oxygen in the reaction of **III** with **VIII** can be accounted for by scheme (1). The hydroperoxide is reduced to hydroxytriphenylgermane, which subsequently reacts with the starting alcoholate to form tri-*tert*-butoxytriphenylgermyloxytitanium [reactions (7)–(9)]:

$$\begin{array}{rcl} Ph_{3}GeOOH + Ti(OBu-t)_{4} \\ &\longrightarrow t-BuOH + Ph_{3}GeOOTi(OBu-t)_{3}, & (7) \\ & \mathbf{A} \\ & \mathbf{A} + Ph_{3}GeOOH \\ & \longrightarrow Ph_{3}GeOTi(OBu-t)_{3} + Ph_{3}GeOH + O_{2}, & (8) \end{array}$$

$$\longrightarrow$$
 Ph₃GeOTi(OBu-t)₃ + t-BuOH. (9)

If reactions (7)–(9) are the major pathway of the reaction of Ph_3GeOOH with III, *t*-BuOH should be released in an amount of ~1 mol. As will be shown below, the subsequent transformations of titanium triphenylgermyloxy derivative yield hexaphenylgermanoxane and alcoholate III.

 $Ph_3GeOH + Ti(OBu-t)_4$

Thus, if there are no energetically favorable pathways for intramolecular decomposition of peroxides **A**, their further reaction with hydroperoxides results in the reduction of the hydroperoxides and release of oxygen.

Tables 1 and 2 show that the hydroperoxide reduction products R'OH were detected both in the free state and (to a greater extent) in the metal-bound

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form. Special experiments showed that triphenylmethanol, 2-phenylpropan-2-ol, and 1,1-diphenylethanol enter exchange reactions with **II** and **III**. Under the conditions of the hydrolysis and in the course of the reactions, these alcohols are partially dehydrated to alkenes. The reactions of the alkenes with the system alcoholate **III**-hydroperoxide **IV** or **V** account for the presence of acetophenone and benzophenone, respectively, in the reaction products [17].

The triphenylelement hydroxides formed by decomposition of the titanium peroxy compounds react further with metal alcoholates. The reaction pathway depends on the structure of the alkoxy group. From the reactions of $(n-BuO)_4Ti$ with Ph₃EOOH (**VII**, **VIII**), we isolated tetrakis(triphenylsiloxy)- and tetrakis(triphenylgermyloxy)titanium, respectively. It is known [14, 18–20] that alcoholate **II** enters an exchange reaction with Ph₃EOH to form (Ph₃EO)₄Ti:

$$(BuO)_4Ti + 4Ph_3EOH > (Ph_3EO)_4Ti + 4BuOH,$$
 (10)
D, **E**
 $E = Si$ (**D**), Ge (**E**).

Variation of the reactant ratio does not lead to formation of unsymmetrical triphenylsiloxyalkoxy derivatives of titanium [20].

Compounds **D** and **E** are colorless finely crystalline extremely thermostable substances moderately soluble (especially **D**) in benzene. In the reaction under consideration, $(Ph_3SiO)_4Ti$ starts to form 25–30 min after the start of the reaction, and its yield is ~0.20 mol, i.e., almost 0.80 mol of Ph_3SiOH is bound to Ti. However, Ph_3SiOH is formed by decomposition of the titanium-containing peroxy compound [reactions (3), (4)], and in the process alcoholate **II** is removed from the reaction sphere. Therefore, reaction (7) is improbable.

We assumed that compound **D** could form in the last steps by the reaction of $[(BuO)_2TiO]_x$ with Ph₃SiOH [Eq. (11)], as it is known that the Ti–O–Ti bonds in titanoxanes are cleaved in the presence of Ph₃SiOH with the formation of tetrakis(triphenylsiloxy)titanium [20]:

$$[(BuO)_{2}TiO]_{x} + 4Ph_{3}SiOH$$

$$\longrightarrow (Ph_{3}SiO)_{4}Ti + 2BuOH + H_{2}O.$$
(11)

Water can hydrolyze the BuO-Ti bonds.

To check this hypothesis, the residue obtained by the reaction of alcoholate **II** with hydroperoxide **VII** after the separation of $(Ph_3SiO)_4Ti$ was treated with triphenylhydroxysilane. In so doing, we assumed that at least a half of Ti was in the form of $(BuO)_2$ TiO. In 12 h, we obtained an additional 0.49-mol crop of **D**. The yield of 1-butanol in the volatile fraction reached 2.5 mol.

Triphenylhydroxygermane also reacts with $(BuO)_4Ti$ or $[(BuO)_2TiO]_x$ to form tetrakis(triphenyl-germyloxy)titanium. However, this reaction is extremely slow and mainly occurs after the removal of the major fraction of the solvent; 0.06 to 0.16 mol of $(Ph_3GeO)_4Ti$ (E) is formed.

The IR spectra of the isolated and independently synthesized (Ph₃SiO)₄Ti samples are identical and consistent with the published data [18, 21]. The spectra of the (Ph₃GeO)₄Ti samples isolated from the reaction of **II** with **VIII** and prepared by an independent synthesis are also identical and similar to the IR spectrum of the Si derivative. The spectra contain bands of the Ge–Ph bonds (1100, 1440 cm⁻¹), and also a very strong band at 835 cm⁻¹ and a medium-intensity band at 870 cm⁻¹. By analogy with the spectrum of D [18], these bands can be assigned to v_{as} (Ge–O–Ti) and v_{as} (Ti–O–Ge), respectively. We found no published data on the IR spectra of **E**.

The reaction of (t-BuO)₄Ti with **VII** yields mixed alkoxy(siloxy) titanium derivatives; their hydrolysis yields Ph₃SiOH. In the reaction with **VIII**, up to 0.40 mol of (Ph₃Ge)₂O (isolated before hydrolysis) is formed (Table 1). We assumed that Ph₆Ge₂O could form by disproportionation of the mixed titanium alcoholate by reactions (8) and (9) and by decomposition of the disproportionation product [reactions (12), (13)].

$$2Ph_{3}GeOTi(OBu-t)_{3}$$

$$\longrightarrow (Ph_{3}GeO)_{2}Ti(OBu-t)_{2} + Ti(OBu-t)_{4}, \quad (12)$$

$$(Ph_{3}GeO)_{2}Ti(OBu-t)_{2}$$

$$\longrightarrow (Ph_{3}Ge)_{2}O + [(t-BuO)_{2}TiO]_{x}. \quad (13)$$

Also, hexaphenyldigermanoxane and alcoholate III can form by intermolecular condensation of the titanium germyloxy compound followed by decomposition of titanoxane \mathbf{F} by reactions (14) and (15):

$$\xrightarrow{2(t-BuO)_3 \text{TiOGePh}_3} \longrightarrow Ph_6 Ge_2 O + (t-BuO)_3 \text{TiOTi}(OBu-t)_3, \qquad (14)$$

$$\mathbf{F}$$

$$\mathbf{F} \longrightarrow (t-\mathrm{BuO})_4\mathrm{Ti} + [(t-\mathrm{BuO})_2\mathrm{TiO}]_x.$$
 (15)

Formation of binuclear oxides by reaction (14) is one of the pathways of decomposition of metal alkoxides [22]. Disproportionation of titanium compounds to $Ti(OR)_4$ was demonstrated by the example of hexakis(trimethylsiloxy)titanoxane [23].

To confirm the occurrence of reactions (12)–(15), we performed the reaction of **III** with triphenylhydroxygermane in benzene (20°C) at a reactant ratio of 1:1 and obtained 0.46 mol of hexaphenyldigermanoxane and 1.09 mol of t-BuOH. Distillation of the benzene solution after the separation of the germanoxane gave 0.42 mol of $Ti(OBu-t)_4$. The reaction of III with Ph_3GeOH in a 1:16 ratio gave 4.0 mol of t-BuOH and 2.24 mol of Ph₆Ge₂O; 10.87 mol of Ph₃GeOH remained unchanged. These results confirm the lack of the catalytic effect of the titanium alcoholate on the formation of hexaphenyldigermanoxane. Hence, (triphenylgermyloxy)tri-tert-butoxytitanium is unstable. Similar transformations (12)-(15) occur in the reaction of triphenylgermyl hydroperoxide with alcoholate III.

EXPERIMENTAL

The IR spectra were recorded on Specord IR-75 and Specord M-80 spectrophotometers (thin liquid film between KBr windows). The ESR spectra were taken on a Bruker ER-200D-SRC spectrometer equipped with an ER-4105DR double cavity (operating frequency ~9.5 GHz) and an ER-4111VT temperature control unit. In determination of the g factors, diphenylpicrylhydrazyl was used as reference. Chromatographic analysis of reaction products in the liquid phase was performed with a Tsvet-2-65 chromatograph equipped with a flame ionization detector; the carrier gas was Ar. High-boiling products (benzyl alcohol, benzaldehyde, phenol, acetophenone, α-methylstyrene, benzophenone, 2-phenylpropan-2-ol, 1,1-diphenylethanol, 1,1-diphenylethylene, etc.) were analyzed on a 1200×3 -mm column (stationary phase 15% Reoplex-400 on Chromaton N-AW-DMCS, 100-230°C). Acetone, butanol, butanal, tert-butanol, and tert-butyl hydroperoxide were analyzed on an LKhM-80 chromatograph equipped with a 1200×3 -mm column; carrier gas He, stationary phase 15% dinonyl phthalate on Chromaton N-AW-DMCS, 40-80°C. Titanium tetra-*tert*-butylate was analyzed on a $2400 \times$ 3-mm column, stationary phase 15% Apieson L on Chromaton N-AW-DMCS, 180°C. The chromatograms were treated by the method of external reference, with authentic samples used in each case. All manipulations with the metal-containing compounds were performed under dry deoxygenated argon.

The content of *tert*-butoxy groups was determined by the Denigès method [24], and the content of aliphatic acids in nonvolatile residues, according to [25]. Carbonyl compounds were identified in the form of 2,4-dinitrophenylhydrazones by the melting points and by TLC (comparison of R_f values with those of authentic samples). The sorbent (Silpearl) was coarseporous silica gel on aluminum foil (Silufol UV-254); eluent benzene or benzene–diethyl ether, 9 : 1. The amount of the released oxygen was determined from the weight of benzoic acid formed by the reaction of O_2 with benzaldehyde [26]. The amount of hydroperoxides was determined by iodometric titration.

Titanium tetra-*tert*-butylate and tetrabutylate were prepared by treatment of TiCl₄ with the corresponding butyl alcohol in the presence of NH₃ [27]; Ti(OBu-t)₄, bp 82–83°C (2 mm Hg), n_D^{20} 1.4420 [14]; Ti(OBu-n)₄, bp 138–140°C (1 mm Hg), n_D^{20} 1.4918 [14].

Ph₃SiOOH was prepared from Ph₃SiCl and 96% hydrogen peroxide; mp 110–111°C [28]. Ph₃GeOOH was prepared similarly from Ph₃GeBr; mp 136°C [29]. 1-Hydroperoxy-1,1-diphenylethane and triphenylmethyl hydroperoxide were prepared from the corresponding alcohols by the reaction with 90% hydrogen peroxide in the presence of concentrated sulfuric acid. Ph₂C(OOH)Me: colorless crystals (from petroleum ether), mp 82°C [30]; Ph₃COOH: pale yellow lustrous crystals (from hexane), mp 83–84°C [30]. The activity of all the peroxides synthesized was no less than 99.0%. The concentration of *tert*-butyl and cumyl hydroperoxides used in the study was no less than 99.6–99.8%.

Reactions of hydroperoxides with titanium alcoholates (general procedure). Titanium alcoholate was added to the hydroperoxide in benzene. The mixture was kept at room temperature until the reaction for peroxide became negative. The solvent and volatiles were condensed in a trap cooled with liquid nitrogen. The nonvolatile residue was hydrolyzed with 10% sulfuric acid in ether; the reaction products were thoroughly extracted with ether. The volatile fractions and ether hydrolyzates were analyzed by GLC. In aqueous acidic hydrolyzates, *t*-BuOH [24] and metal were determined (the metal, by precipitation as hydroxide followed by calcination to TiO_2).

Reaction of cumyl hydroperoxide IV with titanium tetrabutylate, 2 : 1. A mixture of 0.58 g of $Ti(OBu)_4$ and 0.52 g of PhCMe₂OOH in 9 ml of benzene was kept at room temperature for 24 h; 16 ml of O₂ was released (normal conditions). The reaction solution was bright yellow. In the condensate of volatile reaction products, we found 0.056 g of PrCHO, 0.27 g of BuOH, 0.12 g of PhCMe₂OH, and 0.008 g of PhC(O)Me; formaldehyde was identified qualitatively as 2,4-dinitrophenylhydrazone. The residue was a light yellow resinous mass. In the ether extract after the hydrolysis, we found 0.09 g of BuOH, 0.02 g of PrCHO, 0.28 g of PhCMe₂OH, 0.014 g of PhC(O)Me, and 0.01 g of PhC(Me)=CH₂. The residue

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from a parallel run was analyzed for formic and butyric acids [25]. The xylene solution after the titration with alkali was separated, and the alkaline solution was concentrated. The residue was acidified with H_2SO_4 , and the products were extracted with diethyl ether. After the treatment with diazomethane, methyl butyrate and methyl formate were identified. Found, g: HCOOH 0.001 and PrCOOH 0.02.

Reaction of titanium tetra-tert-butylate III with 1-hydroperoxy-1,1-diphenylethane V, 1:2. To a solution of 0.73 g of Ph₂(Me)COOH in 10 ml of benzene, we added 0.58 g of $(t-BuO)_4$ Ti. Oxygen was released. Within 1 min after mixing the components, the mixture became lemon-yellow, and within 15 min, red-brown. In the condensed solvent, we found 0.32 g of *tert*-butyl alcohol and 0.02 g of acetophenone. The residue was a dark brown mobile mass, which was hydrolyzed as described above. In the ether extract, we determined chromatographically 0.11 g of t-BuOH, 0.31 g of Ph₂C(OH)CH₃, 0.028 g of PhC(O)CH₃, 0.089 g of $Ph_2C=CH_2$, 0.009 g of $Ph_2C=O$, and 0.016 g of PhOH. In the hydrolyzate, we found by iodometric titration 0.09 g of unchanged $Ph_2(Me)$. COOH. 1-Hydroperoxy-1,1-diphenylethane was identified by products of its acid decomposition [phenol and PhC(O)Me] in the presence of p-toluenesulfonic acid [31].

Reaction of Ph₃COOH (VI) with (BuO)₄Ti, 1 : 1. No oxygen evolution was observed on mixing 0.83 g of triphenylmethyl hydroperoxide and 1.02 g of Ti(OBu)₄ in 10 ml of benzene. The test for peroxide compounds became negative within 30 min. The orange-red reaction solution was allowed to stand for 24 h; the crystalline precipitate was filtered off. It was identified by elemental analysis as triphenylmethyl peroxide. Found, %: C 87.96; H 5.86. $C_{38}H_{30}O_2$. Calculated, %: C 88.03; H 5.79. Yield 0.09 g; melting point of the product and of its mixture with an authentic sample 183°C.

In the volatile fraction of the filtrate, we found 0.28 g of BuOH and 0.06 g pf PrCHO. Along with butanal, we also identified formaldehyde by TLC in the form of 2,4-dinitrophenylhydrazone.

The residue (yellow oily mass) was treated as described above. In the ether extract, we found 0.38 g of butanol, 0.04 g of butanal, 0.07 g of phenol, and 0.22 g of benzophenone (melting point of 2,4-dinitrophenylhydrazone and of the mixture with an authentic sample 240° C).

In a separate experiment, we found 0.02 g of butyric acid and 0.002 g of formic acid (determined as methyl esters [25]). In a parallel run, the residue after the separation of triphenylmethyl peroxide and volatiles was steamdistilled. From the bottoms, we isolated 0.33 g of Ph_3COH , mp 160°C.

Reaction of triphenylsilyl hydroperoxide VII with titanium tetrabutylate, 1:1. To 0.38 g of $(BuO)_4$ Ti in 7 ml of benzene, we added 0.32 g of Ph₃SiOOH. After mixing the components, the reaction mixture became orange-red, and in 15 min a colorless crystalline precipitate formed; the test for peroxy compounds was negative. The mixture was allowed to stand for 20 h for more complete precipitation. The precipitate was filtered off and washed with small portions of hexane. (Ph₃SiO)₄Ti was obtained; yield 0.23 g. Found, %: C 75.92; H 5.63; Si 9.58; Ti 4.42 [18]. C₇₂H₆₀O₄Si₄Ti. Calculated, %: C 75.26; H 5.23; Si 9.76; Ti 4.17.

After the separation of $(Ph_3SiO)_4Ti$, in the condensed solvent we found chromatographically 0.12 g of butyl alcohol and 0.02 g of butanal; propene was identified qualitatively. On treatment of a part of the condensate with 2,4-dinitrophenylhydrazine, we obtained a precipitate of hydrazones (derived from butanal and formaldehyde; TLC). The mixture of 2,4-dinitrophenylhydrazones was separated by column chromatography (silica gel, eluent benzene–ether, 18 : 1). 2,4-Dinitrophenylhydrazones of butanal (mp 120°C) and formaldehyde (mp 163°C) were isolated. The melting points were consistent with the published data. The presence of formaldehyde was also proved by preparation of its dimedone derivative (mp 189°C).

The residue (colorless solid) was hydrolyzed with 10% H_2SO_4 ; the reaction products were extracted with ether. In the ether extract, we found 0.12 g of 1-butanol, 0.008 g of PhOH, and 0.048 g of butyric acid [25]. The solvent was removed; in the dry residue we found 0.08 g of Ph₃SiOH and [Ph₂SiO]_n [32].

The color of the aqueous layer did not disappear after extraction with ether but disappeared after treatment with potassium permanganate, which suggests the presence of readily oxidizable substances, probably phenol oxidation products.

Quantitative determination of propene. The volatiles from a separate experiment were condensed in a trap that was preliminarily filled with HCl-saturated benzene. After completion of the distillation, the contents were thawed, allowed to stand for 1 h, and washed with a dilute sodium carbonate solution to remove excess HCl. The isopropyl chloride formed in the process (0.05 g) was determined chromatographically.

Reaction of triphenylgermyl hydroperoxide VIII

with alcoholate **II** was performed similarly. From the reaction of 0.43 g of Ph₃GeOOH and 0.44 g of Ti(OBu)₄, we isolated 0.27 g of (Ph₃GeO)₄Ti. Colorless crystalline substance; does not melt up to 360° C; moderately soluble in benzene. Found, %: C 65.50; H 4.64; Ge 21.89; Ti 3.83 [18]. C₇₂H₆₀Ge₄O₄Ti. Calculated, %: C 65.16; H 4.53; Ge 21.87; Ti 3.61.

Reaction of Ph₃GeOOH (VIII) with (t-BuO)₄Ti, **1:1.** To 0.58 g of $(t-BuO)_4$ Ti in 15 ml of benzene, we added 0.59 g of Ph₃GeOOH. Immediately after mixing the components, the reaction mixture became lemon-yellow, and oxygen evolved (12.5 ml, normal conditions). The test for peroxide oxygen became negative within 15 min. The crystalline precipitate was filtered off; its mixture with an authentic sample of Ph₆Ge₂O showed no melting point depression (mp 185°C). Yield of Ph₆Ge₂O (before hydrolysis) 0.42 g. In the condensate of the volatile fraction, we found 0.11 g of tert-butyl alcohol and 0.27 g of titanium tetra-tert-butylate; an epoxide was detected qualitatively [33]. By treatment of a part of the condensate with $BF_3 \cdot Et_2O$, the epoxide was isomerized into a carbonyl compound [34], which was identified in the form of 2,4-dinitrophenylhydrazone. This hydrazone (derived from isobutyraldehyde; mp 186°C) was isolated by column chromatography (silica gel, eluent benzene–ether, 18:1).

The residue (viscous orange mass) was hydrolyzed with 10% H₂SO₄; the hydrolysis products were extracted with ether.

In the extract we found 0.17 g of *tert*-butyl alcohol and 0.01 g of PhOH. After removal of the ether, the residue was treated with boiling hexane. The insoluble residue was Ph_6Ge_2O (0.04 g), mp 184°C. After evaporation of the hexane filtrate, 0.06 g of Ph_3GeOH was obtained; mp 135°C. The samples of the isolated Ph_6Ge_2O and Ph_3GeOH showed no melting point depression on mixing with authentic samples.

In the aqueous acidic layer, we found 0.06 g of *tert*-butyl alcohol [24].

In the similar reaction of titanium tetra-*tert*-butylate with hydroperoxide **VIII** (component ratio 1 : 2), we obtained 0.64 mol of oxygen and 0.88 mol of hexaphenyldigermanoxane (per mole of the starting titanium alcoholate).

Reaction of triphenylhydroxygermane with titanium tetra-*tert***-butylate.** To 2.27 g of Ph_3GeOH dissolved in 20 ml of benzene, we added with vigorous stirring 2.40 g of titanium tetra-*tert*-butylate. A precipitate started to form 5 min after mixing the components. The solution was allowed to stand for 24 h. The precipitate (1.87 g) was filtered off. The sample and its mixture with an authentic sample of Ph_6Ge_2O had mp 186°C. The filtrate was distilled under reduced pressure, and 1.01 g of Ti(OBu-*t*)₄ was recovered; bp 73°C (1.5 mm Hg), n_D^{20} 1.4420, which is consistent with the published data [14].

In a parallel run, in the volatile fraction of the reaction products we determined chromatographically 0.54 g of *t*-BuOH.

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