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Titanium(IV) *tert*-Butoxide–*tert*-Butyl Hydroperoxide System as Oxidant for C–H Bonds in Hydrocarbons and Oxygen-containing Compounds

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Abstract—The system Ti(IV) tetra-*tert*-butoxide–*tert*-butyl hydroperoxide in mild conditions (20°C) oxidizes C–H bonds of methyl (toluene), methylene (hexane, ethylbenzene, benzyl ethyl ether), and methine (1,1-diphenylethane, triphenylmethane) groups. The role of oxidant is played by the oxygen generated by the system. The process involves free radicals and produces hydroperoxides and Ti(IV) peroxides. The latter decompose both with preservation and decomposition of the hydrocarbon skeleton.

Previously we showed [1–5] that the Al(OBu-*t*)3–*t*-BuOOH system effectively and in mild conditions (20°C) oxidizes C–H bonds in alkanes, alkylarenes, as well as oxygen-containing functional derivatives (aldehydes, ketones, saturated ethers and esters, etc.). The fact that best oxidized are C–H bonds in the allyl, benzyl, and benzhydryl radicals points to a homolytic nature of the processes. The formation of carbon-centered and peroxyl radicals from the substrates was confirmed by ESR [6]. At present we are searching for new mild oxidants comprising other metals, both main-group and transition. Therewith, we set ourselves the task to establish the role of the metal, common features of the processes, and reaction centers on the system and substrates.

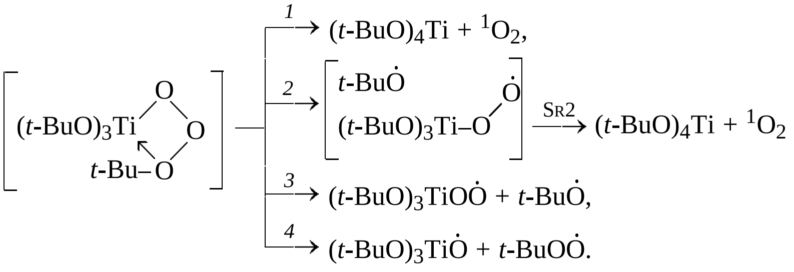
It is known that aluminum and Ti(IV) alkoxides sometimes exhibit similar chemical properties. Thus, their reactions with alcohols, carbonyl compounds, and carboxylic acid anhydrides and halides occur in a similar fashion. Both metals have vacant *p* and *d* orbitals. Therefore, one may expect that reactions of aluminum and Ti(IV) alkoxides will similarly react with hydroperoxides. The aim of the present work was to explore the oxidative power of the Ti(IV) tetra-*tert*-butoxide (**I**)–*tert*-butyl hydroperoxide (**II**) system. The reaction of alkoxide **I** with hydroperoxide **II** in a 1 : 2 ratio in benzene at room temperature is accompanied by evolution of oxygen whose yield attains 0.85–0.90 mol/mol **I** [7]. Distillation after reaction completion recovered ~0.80 mol of Ti(IV) alkoxide [Eq. (1)].

$$\mathrm{Ti(OBu\text{-}}t)_4 + 2t\text{-}\mathrm{BuOOH},$$
$$\mathrm{O_2} + 2t\text{-}\mathrm{BuOH} + \mathrm{Ti(OBu\text{-}}t)_4. \qquad (1)$$

When the **I** : **II** ratio was increased to 1 : 10, the yield of oxygen was 4.2 mol. No solvent oxidation products were found.

The reaction between the components of the systems involves formation of Ti(IV) peroxide and trioxide, like in the system comprising aluminum alkoxide [6, 8]. Decomposition of the trioxide results in oxygen evolution (therewith, Ti(IV) alkoxide is regenerated [7]) and formation of oxygen-centered alkoxyl and peroxyl radicals [Scheme (2)].

$$(t\text{-}\mathrm{BuO})_4 + t\text{-}\mathrm{BuOOH} \rightleftarrows t\text{-}\mathrm{BuOH} + (t\text{-}\mathrm{BuO})_3\mathrm{TiOOBu}\text{-}t,$$
$$(t\text{-}\mathrm{BuO})_3\mathrm{TiOOBu}\text{-}t + t\text{-}\mathrm{BuOOH}$$
$$t\text{-}\mathrm{BuOH} + (t\text{-}\mathrm{BuO})_3\mathrm{TiOOOBu}\text{-}t.$$



(2)

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Roughly half the oxygen was fixed in the singlet state. It undergoes singlet–triplet transition in the presence of oxygen-centered radicals [9].

We previously showed that the **I**–**II** system oxidizes alkylarenes [7] but did not study these reactions in detail. In the present work we explored the reaction of this system with C–H bonds of alkanes, alkylarenes, and certain oxygen-containing saturated derivatives. All reactions were performed at room temperature in benzene or in the substrate to be oxidized at the **I** : **II** ratio of 1 : 2. The working concentration of alkoxide **I** was varied within 0.05–0.30 M. The starting compounds were hydrocarbons having methyl, methylene, and methine C–H bonds, such as hexane, toluene, ethylbenzene, 1,1-diphenylethane, and triphenylmethane.

After oxidation of hexane, the volatile fraction contained (moles per mole titanium alkoxide) : *t*-BuOH (2.88), 2-hexanone (0.10), and 3-hexanone (0.10), and the nonvolatile residue after hydrolysis contained *t*-BuOH (2.92), 2-hexanone (0.02), 3-hexanone (0.03), 2-hexanol (0.05), and 3-hexanol (0.03). In addition, 0.03–0.04 mol of a mixture of carboxylic acids (acetic, propanoic, butanoic) was found, which implies destructive oxidation of hexanones [1]. Roughly half the oxygen evolves free.

Data on the reaction products of the **I**–**II** system with alkylarenes are listed in Table 1. As seen, here, too, carbonyl compounds, alcohols, or their transformation products are formed. Moreover, much hydroperoxides were found. It should be noted that in toluene and ethylbenzene no free oxygen was found, as it is almost completely consumed for oxidation of solvent C–H bonds.

The composition of oxidation products points to a radical character of the process. Let us use the example of ethylbenzene to consider the possible reaction pathways. Under the action of oxygen on C–H bonds, both carbon-centered and hydroperoxide radicals whose reaction may result in the oxidation of the α-phenylethyl radical to acetophenone or in hydroperoxide formation [Eq. (3)].

$$\mathrm{PhCH_2Me + O_2 \longrightarrow [Ph\dot{C}HMe + \dot{O}OH] \longrightarrow \left\{ \begin{array}{l} \rightarrow PhCOMe + H_2O, \\ \rightarrow PhCH(OOH)Me. \end{array} \right.} \qquad (3)$$

The second way of hydroxide formation may involve oxidation initiated by oxygen-centered radicals with intermediate formation of alkyl peroxide radicals [Eq. (4)].

$$\begin{aligned} &\mathrm{PhCH_2Me + R\dot{O} \xrightarrow[-ROH]{} Ph\dot{C}HMe} \\ &\mathrm{\xrightarrow{O_2} PhCH(O\dot{O})Me} \\ &\mathrm{\xrightarrow{PhCH_2Me} PhCH(OOH)Me,} \qquad (4) \end{aligned}$$

R = *t*-Bu, *t*-BuO, $(t\text{-BuO})_3$Ti, $(t\text{-BuO})_3$TiO.

In our opinion, the latter pathway is more probable [6]. Disproportionation of the alkyl peroxide radicals by the Russel mechanism [10] [Eq. (5)] gives rise to simultaneous formation of an alcohol and a ketone.

$$\mathrm{2PhCH(O\dot{O})Me \longrightarrow PhCOMe + PhCH(OH)Me + O_2.} \quad (5)$$

The latter equation also explains why the yield of oxidation products in the reaction of compound **I** [0.05 mol l^{-1}] with hydroperoxide **II** in ethylbenzene is more than 1 mol. However, it should be noted that as the concentration of alkoxide **I** from 0.30 to 0.05 M in the case of Ph_2CHCH_3 and Ph_3CH, the conversion of the substrates was decreased.

The third pathway that leads to acetophenone involves reaction of 1-hydroperoxy-1-phenylethane with alkoxide **I** and decomposition of the Ti(IV) peroxide according to Eq. (6).

$$\begin{aligned} &\mathrm{PhCH(OOH)Me + Ti(OBu\text{-}}t)_4 \\ &\xrightarrow[-t\text{-BuOH}]{} \underset{\textbf{IV}}{(t\text{-BuO})_3\mathrm{TiOOCH(Me)Ph}} \\ &\longrightarrow (t\text{-BuO})_3\mathrm{TiOH + PhCOMe.} \qquad (6) \end{aligned}$$

Moreover, peroxide **IV** undergoes rearrangement accompanied by the decomposition of the titanium alkoxide to acetaldehyde and metal phenoxide.

$$\begin{aligned} &\textbf{IV} \longrightarrow (t\text{-BuO})_3\mathrm{TiOCH(Me)OPh} \\ &\longrightarrow (t\text{-BuO})_3\mathrm{TiOPh + MeCHO.} \qquad (7) \end{aligned}$$

The same process takes place in the oxidations of toluene and triphenylmethane. In the latter case, this is a major reaction pathway.

Table 1. Reaction products of alkylarenes with the Ti(OBu-*t*)$_4$–*t*-BuOOH system (molar ratio 1 : 2) [initial concentration of Ti(OBu-*t*)$_4$ 0.3 M, 20°C] (moles per mole titanium alkoxide)

Reaction products[a]	Alkylarenes				
	$PhCH_3$	$PhCH_2CH_3$		Ph_2CHCH_3	Ph_3CH
	Volatile reaction products				
t-BuOH	2.89	3.64	2.42[b]	2.91[b]	1.88[b]
Carbonyl compound	PhCHO[c]	PhCOMe[d]		PhCOMe	–
	0.15	0.07	0.05	0.02	
	Hydrolysis products of nonvolatile residue[e]				
t-BuOH	2.98	2.32	3.46	2.43	4.08
Carbonyl compound	PhCHO[f]	PhCOMe		Ph_2CO	Ph_2CO
	0.05	0.34	0.11	0.02	0.12
Alcohol	$PhCH_2OH$	PhCH(OH)Me		$Ph_2C(OH)Me$	
	0.06	0.12*	0.02	0.08	–
PhOH	0.04	0.03	–	–	0.13
Hydroperoxide	$PhCH_2OOH$	PhCH(OOH)Me		Ph2C(OOH)Me	Ph_3COOH
	0.16	0.25	0.25	0.39	0.18
Alkylarene (starting)	h	h	0.54	0.48	0.60
Carboxylic acid	PhCOOH 0.40	CH_3COOH		–	–
	HCOOH 0.07	0.08	i		

[a] Averaged results. [b] The reactions were performed in benzene; **I** : **II** : alkylarene = 1 : 2 : 1. Oxygen evolution was observed. [c] Formaldehyde was qualitatively detected. [d] Acetaldehyde was qualitatively detected in condensates and hydrolyzates. [e] 1 mol of titanium was used in all experiments. [f] Butyl benzoate (0.01 mol) was found. [g] Styrene (0.04 mol) was found. [h] Solvent alkylarene. [i] Not found.

Thus, titanium peroxides can decompose by Eqs. (6) and (7). Aldehydes are partially oxidized into acids [Eq. (8)].

$$-\!\!\!<\text{TiOOBu-}t + \text{RCHO} \longrightarrow [-\!\!\!<\text{TiOCH(R)OOBu-}t]$$
$$\longrightarrow -\!\!\!<\text{TiOCOR} + t\text{-BuOH}, \qquad (8)$$
$$\text{R = H, Me, Ph.}$$

From Table 1 it follows that the fraction of carbonyl compounds is always larger that the fraction of alcohol. This result is probably explained both by that there are several pathways of formation of aldehydes and ketones, as well as by partial oxidation of alcohols.

As the model reaction we performed reaction of the **I**–**II** system with benzyl alcohol (1 : 1 : 1) in benzene. The alcohol conversion was 67%. Therew ith, we isolated 0.43 mol of benzaldehyde, 0.02 mol of benzyl benzoate, and 0.15 mol of benzoic acid. These results provide evidence for our suggestion.

$$\text{Ti(OBu-}t)_4 + \text{PhCH}_2\text{OH} + t\text{-BuOOH}$$
$$\longrightarrow 2t\text{-BuOH} + (t\text{-BuO})_2\text{Ti(OCH}_2\text{Ph)OOBu-}t$$
$$\longrightarrow t\text{-BuOH} + \text{PhCHO} + [(t\text{-BuO})_2\text{TiO}]_n. \qquad (9)$$

The oxidation of hexane, as well as of all the alkylarenes studied is described by Eqs. (3)–(7). With alkylarenes, the yields of oxidation products depend on the structure of the substrate. The yields are the highest with toluene and ethylbenzene, on account of the formation of benzyl radicals. The lower conversions of 1,1-diphenylethane and triphenylmethane are explained both by steric reasons and by the lower reactivity of C–H bonds in tertiary alkylarenes [11] and the corresponding peroxyl radicals [12].

It should be noted that (*t*-BuO)$_3$TiOOBu-*t* (**III**) initially formed in the reaction of **I** with **II** does not oxidize hydrocarbons. In special experiments with ethylbenzene, acetophenone was either not found or its quantity was no larger than 0.005 mol. However, as already noted [Eqs (6) and (7)], Ti(IV) peroxides formed from alkoxide **I** and aryl alkyl hydroperoxides generated from starting hydrocarbonds can decompose to give final alkylarene oxidation products. Therewith, destruction of the hydrocarbon skeleton of the substrate is observed.

To find out if titanium-containing peroxides are involved in oxidation, we turned to reactions of Ti(OBu-*t*)$_4$ with 1-hydroperoxy-1-phenylethane and

Table 2. Reaction products of $Ti(OBu\text{-}t)_4$ with hydroperoxides (1 : 1)[a] (moles per mole titanium alkoxide; benzene, 20°C, 24 h)

Reaction products[a]	Hedroperoxide		
	PhCH(OOH)Me	$Ph_2C(OOH)Me$	
Volatile reaction products			
t-BuOH	1.99[b]	1.50[b]	1.75[c]
PhCOMe	0.06	0.07	0.06
Hydrolysis products of nonvolatile residue[d]			
t-BuOH	1.68	2.29	2.09
PhCOMe	0.11	–	–
Ph_2CO	–	0.02	0.04
Alcohol	PhCH(OH)Me	$Ph_2C(OH)Me$	
	0.09	0.48	0.18
PhOH	0.05	0.06	0.06
Alkene	$PhCH{=}CH_2$	$Ph_2C{=}CH_2$	
	0.02	0.27	0.35
CH_3COOH[e]	0.05	–	–
Hydroperoxide (starting)	0.67	0.05	0.22

[a] Averaged results. [b] Concentration of ROOH 0.30 M. [c] Concentration of ROOH 0.05 M. [d] 1 mol of titanium was used in all experiments. [e] Acetaldehyde was qualitatively detected in the volatile fraction.

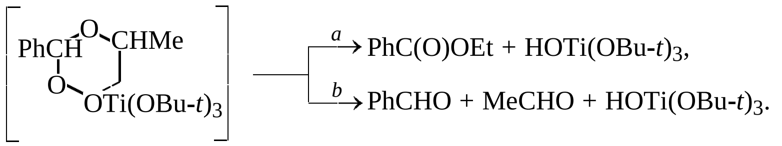
1-hydroperoxy-1,1-diphenylethane (Table 2). From a comparison of the data in Tables 1 and 2 it follows that the qualitative composition of the products formed by the oxidation with the **I**–**II** system of ethylbenzene and 1,1-diphenylethane and the products of the reactions of their corresponding hydroperoxides with Ti(IV) alkoxide is the same. Both on the oxidation of ethylbenzene with the **I**–**II** system and on the reaction of 1-hydroperoxy-1-phenylethane with compound **I** we isolated acetophenone, 1-phenyl-1-ethanol, as well as phenol, acetic acid, and acetaldehyde, which provides evidence for the above suggestions. However, quantitative analysis, especially in the case of ethylbenzene, leaves rooms for other pathways leading the to ketone and alcohol. Thus, in the oxidation of ethylbenzene with the **I**–**II** system, a total of 0.55 mol of acetophenone and 1-phenyl-1-ethanol and 0.25 mol of 1-hydroperoxy-1-phenylethane were found. Upon the reaction of 1-hydroperoxy-1-phenylethane with alkoxide **I** in the same conditions, we found ~0.30 mol of hydroperoxide transformation products and about 0.70 mol of unreacted hydroperoxide. These findings provide evidence for the presence of several oxidation pathways [Eqs. (5)–(7)].

As seen from Table 2, the major product of the reaction of 1-hydroperoxy-1,1-diphenylethane with alkoxide **I** is a tertiary alcohol. Presently its formation pathways are unclear. Adam *et al.* [13] in their work on Ti(IV)-catalyzed epoxidation of alkenes with singlet oxygen showed that hydroperoxides are reduced to the corresponding alcohols under the action of titanium alkoxides [$Ti(OPr\text{-}i)_4$, $Ti(OBu\text{-}t)_4$]. Such process may occur in the system in study, but this transformation still remains to be explained convincingly. Alkenes are formed by dehydration of the corresponding alcohols.

To find out if C–H bonds can be oxidized not only in hydrocarbons, but also in their derivatives, we reacted the **I**–**II** system with benzyl ethyl ether. The reaction in benzene (20°C) at a **I** : **II** : $PhCH_2OEt$ ratio of 1 : 2 : 1 resulted in isolation of the following volatile products (moles per mole titanium alkoxide): *t*-BuOH (3.61), benzaldehyde (0.11), benzyl alcohol (0.08), ethyl benzoate (0.09), acetaldehyde, and O_2 (qualitatively). Hydrolysis of the nonvolatile residue gave *t*-BuOH (1.77), ethyl benzoate (0.28), benzoic acid (0.04), acetic acid (0.15), and *tert*-butyl benzoate (0.06). The ether conversion is 58%.

The formation of the above compounds can be explained taking into account that the intermediate hydroperoxide resulting from the reaction of the **I**–**II** system with ester C–H bonds [Eqs. (3) and (4)]. Benzyl ethyl ether has two methylene groups available for oxidation. As would be expected, the composition of the reaction products provides evidence for the preferential oxidation of benzyl C–H bonds. Hydroperoxide reacts with alkoxide **I** to form Ti(IV) peroxide. The latter undergoes intramolecular decomposition by two directions, like aluminum peroxides [4] [Eqs. (10) and (11)].

$$PhCH_2OEt + Ti(OBu\text{-}t)_4 + 2t\text{-}BuOOH \longrightarrow 3t\text{-}BuOH + (t\text{-}BuO)_3TiOOCH(Ph)OCH_2Me, \quad (10)$$



(11)

It should be noted that pathway *a* is preferred. Aldehydes are partially oxidized to acyloxy titanium derivatives [Eq. (8)]. The IR spectrum of the reaction residue after removal of the solvent and volatile compounds contains bands (cm^{-1}) characteristic of stretching vibrations of aromatic aldehydes (1710), esters (1720), and carboxylate anions (1590). *tert*-Butoxy(hydroxy)titanium further reacts with the Ti–OBu-*t* bond, as evidenced by the high content of *t*-BuOH in the volatile fraction. *tert*-Butyl benzoate is formed by ethyl benzoate reaction with the **I**–**II** [4, 5], which was confirmed by special experiments.

Thus, the $Ti(OBu\text{-}t)_4$–*t*-BuOOH system effectively oxidizes methylene and methine C–H bonds. Direct oxidation of the methyl group was observed only in toluene, which agrees with the homolytic nature of the process. With benzyl alcohol, intermolecular oxidation with intermediate formation of Ti(IV) peroxide occurs [Eq. (9)], like with aluminum peroxides [14, 15].

In terms of reaction mechanism and products, the **I**–**II** system is similar to the $Al(OBu\text{-}t)_3$–**II** system. The difference is in the rates of oxygen generation and oxidation processes. The induction period of oxygen evolution in the $Al(OBu\text{-}t)_3$–*t*-BuOOH is 20–30 min and in the system with $Ti(OBu\text{-}t)_4$, as little as a few minutes. This difference is probably explained by the monomeric nature of the latter [16] and the lower energy of the Ti–O bond (430 kJ mol^{-1}) [17] compared with Al–O (585 kJ mol^{-1}) [18]. The oxidation process is complete in 1 h on average. However, the fast reaction between components **I** and **II** occasionally results in decreased substrate conversion and evolution of free oxygen, especially when a solvent (benzene) is used.

EXPERIMENTAL

The IR spectra were recorded on a Specord IR-75 instrument in KBr. Chromatographic analysis was performed on a Tsvet-2-65 gas chromatograph with FID, carrier gas argon. Volatile components (acetone, *tert*-butanol) were analyzed on a 2400 × 3 mm column, stationary phase 10% PEGA on a TZKM brick, 55–70°C. Analysis of 2- and 3-hexanones and 2- and 3-hexanols was performed on a 1200x3 mm column, stationary phase 15% Reoplex-400 on Chromaton N-AWDMCS, 90–180°C. High-boiling products (acetophenone, benzophenone, phenol, phenol, styrene, 1,1-diphenylethene, etc.) were analyzed on a 3000 × 3 mm column, packing 5% SE-30 on Inerton-AW, 100–190°C. *tert*-Butyl hydroperoxide was analyzed on an LKhM-80, column 1200 × 3 mm, carrier gas helium, packing 15% dinonyl phthalate on Chromaton N-AW-DMCS, 80°C. Chromatograms were treated by the external calibration technique. All manipulations with Ti(IV) compounds were performed under dry oxygen-free argon.

Analysis of nonvolatile residues for aliphatic acids was performed as described in [19] and for *tert*-butoxy groups, by Deniges [20]. Carboxylic acids were identified as methyl esters after treatment with diazomethane [4]. Carbonyl compounds were identified as 2,4-dinitrophenylhydrazones by melting points and TLC on Silufol UV-254 plates (eluent benzene or benzene–diethyl ether, 9 : 1).

Quantitative analysis for hydroperoxides formed by oxidation of hydrocarbonds was performed by iodometric titration, preliminarily checking that *t*-BuOOH is absent. 1-Hydroperoxy-1-phenylethane and 1-hydroperoxy-1,1-diphenylethane were identified by their acid decomposition products (phenol and the corresponding ketones) in the presence of *p*-toluenesulfonic acid [4].

Titanium *tert*-butoxide was prepared by treatment of $TiCl_4$ with *tert*-butanol in the presence of NH_3 [21], bp 82–83°C (2 mm), n_D^{20} 1.4420 [22]. 1-Hydroperoxy-1-phenylethane and 1-hydroperoxy-1,1-diphenylethane were prepared by treatment of the corresponding alcohols with 90% H_2O_2 in the presence of conc. H_2SO_4 [23]. $Ph_2C(OOH)Me$ is a white crystalline substance, mp 82°C (from petroleum ether) [24]; PhCH(OOH)Me is a viscous colorless liquid, n_D^{27} 1.5210 [25]. The activity of peroxides was no less than 99.6%. The concentration of *tert*-butyl hydroperoxide was no less than 99.6–99.8%.

Oxidation of ethylbenzene with the $Ti(OBu\text{-}t)_4$–*t*-BuOOH system (1 : 1 : 2). A mixture of 0.51 g of $Ti(OBu\text{-}t)_4$, 0.27 g of *t*-BuOOH, and 30 ml of ethylbenzene was allowed to stand at room temperatures for 20 h. The reaction solution was light yellow. No oxygen was evolved. The solvent and volatiles were condensed in a trap cooled with liquid nitrogen. The condensate contained 0.53 g of *t*-BuOH and 0.09 g of acetophenone. Part of the distillate was treated with 2,4-dinitrophenylhydrazine. The 2,4-dinitrophenylhydrazone precipitate was analyzed by TLC. Qualitative analysis detected acetophenone and acetaldehyde derivatives. After removal of acetaldehyde hydrazone with boiling ethanol, an acetophenone derivative was isolated, whose melting point and that the mixed sample were coincident (245°C).

The residue was a dark orange mobile fluid. It was dissolved in diethyl ether and treated with 10% H_2SO_4. The ethereal extract contained 0.10 g of *t*-BuOH, 0.02 g of PhCH(OH)Me, and 0.01 g of MeCOOH.

No phenol and *tert*-butyl hydroperoxide were found. PhCH(Me)OOH (0.08 g) was determined by iodometric titration. For identification of the latter, residual hydrolysis products were dissolved in benzene, and the solution was heated at 60°C for 3 h with a catalytic amount of *p*-toluenesulfonic acid [4]. Phenol, 0.03 g, was determined by chromatography, and acetaldehyde was identified as 2,4-dinitrophenylhydrazone. The formation of these products is evidence for the presence of PhCH(Me)OOH.

Experiments with the other hydrocarbons were performed in a similar way.

Reaction of 1-hydroperoxy-1,1-diphenylethane with alkoxide I. To a solution of 0.75 g of $Ph_2C(Me)OOH$ in 12 ml of benzene, 1.19 g of $Ti(OBu\text{-}t)_4$ was added. In a minute the reaction got stramineous and in 20 min, dark brown. The condensate contained 0.39 g of *t*-BuOH and 0.03 g of PhC(O)Me (identified by TLC as 2,4-dinitrophenylhydrazone).

The residue was a dark brown mobile substance. It was hydrolyzed by the above procedure. The ethereal extract contained (by chromatographic data) 0.43 g of *t*-BuOH, 0.28 g of $Ph_2C(OH)Me$, 0.15 g of $Ph_2C{=}CH_2$, 0.01 g of $Ph_2C{=}O$, and 0.02 g of PhOH. In hydrolyzate, 0.03 g of $Ph_2C(Me)OOH$ was found by iodometric titration. 1-Hydroperoxy-1,1-diphenylethane was identified as described above.

Reaction of benzyl ethyl ether with the $Ti(OBu\text{-}t)_4$–*t*-BuOOH system (1 : 1 : 2). A mixture of 0.27 g of $PhCH_2OEt$, 0.68 g of $Ti(OBu\text{-}t)_4$, and 0.18 g *t*-BuOOH in 7 ml of benzene was allowed to stand for 1 day. The reaction solution got reddish orange. It was concentrated and analyzed by chromatography to find 0.50 g of *t*-BuOH, 0.01 g of PhCHO, 0.02 g of $PhCH_2OH$, 0.03 g of PhC(O)OEt, and 0.08 g of the starting benzyl ethyl ether. Acetaldehyde and benzaldehyde were identified by TLC as 2,4-dinitrophenylhydrazones.

The residue was a yellow tarry substance. It was hydrolyzed with 10% H_2SO_4 and extracted with small portions of diethyl ether. The ethereal extracts contained 0.28 g of *t*-BuOH, 0.06 g of PhC(O)OEt, 0.01 g of $PhCO_2H$ (as methyl ester after treatment with diazomethane), and 0.35 g of the starting benzyl ethyl ether.

The residue from a parallel run was analyzed for acetic acid (found 0.02 g of $MeCO_2H$) [19]. After titration with alkali, the xylene solution was separated, and the alkaline solution was concentrated. The residue was acidified with H_2SO_4 and extracted with diethyl ether. Methyl acetate was identified after treatment of the hydrolyzate with diazomethane.

Peroxide compounds, 0.07 g, were determined by iodometric titration in the presence of Fe^{3+}. The presence of *tert*-butyl perbenzoate among the hydrolysis products was proved by the reaction with aluminum isopropoxide [26].

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