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# Oxidation of β-Dicarbonyl Compounds with *tert*-Butyl Hydroperoxide in the Presence of Vanadyl Acetylacetonate

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**Abstract**—Oxidation of β-dicarbonyl compounds with *tert*-butyl hydroperoxide in the presence of vanadyl acetylacetonate (benzene, 20°C) involves the activated methylene group with intermediate formation of trioxo derivatives and is accompanied by decomposition of carbon skeleton. The oxidation products are carbon dioxide, carboxylic acids, and *tert*-butyl and peroxy esters derived from the latter.

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Reactions of β-diketones with peroxy compounds are governed by both oxidant nature and conditions. For instance, oxidation of alkyl-substituted β-diketones (pentane-2,4-dione derivatives) with hydrogen peroxide in alcoholic medium (20–25°C) in the presence of strong acids leads to the formation of 1,2,4,5-tetraoxanes in 47 to 77% yield [1]. The major products of analogous processes occurring at elevated temperature (80–120°C) are esters formed via subsequent reaction of 1,2,4,5-tetraoxanes with hydrogen peroxide and alcohol. Here, 1,2,4,5-tetraoxane molecule loses two $CH_3C$ fragments [2].

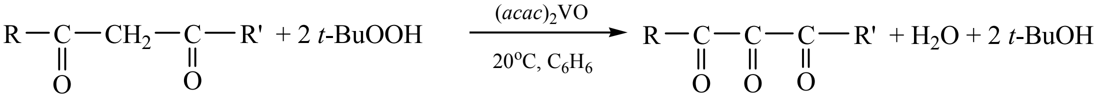
Reactions of hydrogen peroxide with enolizable β-dicarbonyl compounds, such as pentane-2,4-dione, 3-methylpentane-2,4-dione, and ethyl acetoacetate, in the presence of molybdenum(VI) and tungsten(VI) peroxo complexes are accompanied by heat evolution, and they result in the cleavage of the C–C bond between the central carbon atom and the acetyl group. In all cases, the final product is acetic acid, and oxidation of pentane-2,4-dione and ethyl acetoacetate is accom-panied by liberation of carbon dioxide [3–5]. It was found that oxidation of acetylacetone with hydrogen peroxide in the presence of sodium molybdate involves intermediate formation of a complex of metal compound with pentane-2,3,4-trione dihydrate in the coordination sphere of molybdenum(VI) without participation of paramagnetic species [4, 5].

We previously showed that the reaction of vanadyl acetylacetonate (**I**) with *tert*-butyl hydroperoxide (**II**) (benzene, 20°C) at any reactant ratio leads to elimination of the ligand and its oxidation mainly to acetic acid and carbon dioxide through intermediate formation of pentane-2,3,4-trione and diacetyl carbonate [6]. If the ratio $(acac)_2VO$–*t*-BuOOH exceeded 1 : 10, the evolution of oxygen (partly in the singlet state) was observed.

In the present work we examined reactions of β-dicarbonyl compounds with *tert*-butyl hydroperoxide in the presence of vanadyl acetylacetonate (**I**). As substrates we selected compounds containing both aliphatic and aromatic substituents at the carbonyl group: pentane-2,4-dione (**III**), 1-phenylbutane-1,3-dione (**IV**), 1,3-diphenylpropane-1,3-dione (**V**), 1,5-diphenylpentane-1,3,5-trione (**VI**), cyclohexane-1,3-dione (**VII**), and ethyl benzoylacetate (**VIII**). The substrate–*t*-BuOOH molar ratio was varied from 1 : 4 to 1 : 10, depending on the substrate nature, so as to ensure its complete conversion. The ratio vanadyl acetylacetonate (**I**)–*t*-butyl hydroperoxide (**II**) ranged from 1 : 50 to 1 : 100, i.e., the amount of compound **I** may be regarded as catalytic. All reactions were carried out in benzene at room temperature. The reaction was assumed to be complete when carbon dioxide no longer evolved. The reactions of pentane-2,4-dione and cyclohexane-1,3-dione with *t*-BuOOH were exothermic and were complete in 3–4 h. Phenyl ketones **IV** and **VI** reacted at 20°C in 20–24 h, and at 50°C, in 5–6 h. In all cases, the major products were carbon dioxide, carboxylic acids, and *tert*-butyl and peroxy esters (Table 1).

The data in Table 1 show that diketones **III**–**V** react with *tert*-butyl hydroperoxide at the methylene group with decomposition of the carbon skeleton. Although all the examined β-dicarbonyl compounds exist as equilibrium mixtures of ketone and enol tautomers, the structure of the isolated products indicates that they react just as β-diketones. On the other hand, positive test for epoxide ring suggests that *t*-BuOOH reacts with the enol form of the substrates. However, the amount of epoxy derivatives is very small. By analogy with the reaction of vanadyl acetylacetonate with hydroperoxide **II** [6], we presumed the formation of triketones in the first step (Scheme 1).

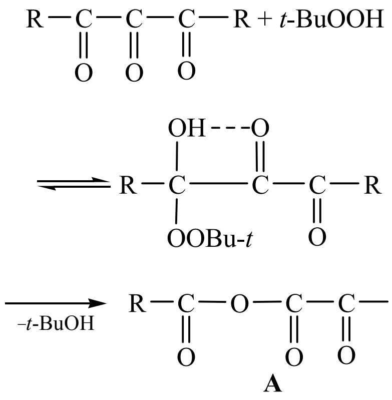
**Scheme 1.**



R = R′ = Me; R = Me, R′ = Ph; R = R′ = Ph.

The subsequent nucleophilic reaction of triketones with *t*-BuOOH (as reported previously for α-diketones [7–9]) should lead to unsymmetrical carboxylic acid anhydrides **A** (Scheme 2; R = R′ was assumed for the sake of simplicity).

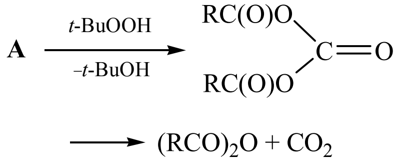
**Scheme 2.**



Intermediate formation of α-hydroxy-α-*tert*-butyldioxy ketone which is then converted into adipic anhydride was detected previously in the reaction of cyclohexane-1,2-dione with *t*-BuOOH [8].

Hydrolysis of unsymmetrical anhydride **A** should produce a mixture of carboxylic acid and α-keto acid. However, all our attempts to detect benzoylformic acid or its ester in the oxidation of diketone **V** were unsuccessful. Furthermore, Schemes 1 and 2 do not rationalize formation of carbon dioxide. We believe that the second C–C bond in anhydride **A** is oxidized to give diacyl carbonate and that the latter undergoes decomposition with liberation of carbon dioxide according to Scheme 3.

**Scheme 3.**



Anhydrides are also capable of reacting with alcohol or hydroperoxide to give esters or peroxy esters, which were detected among oxidation products of all the examined β-dicarbonyl compounds; in addition, free acids may be formed. The latter were identified as

**Table 1.** Products of oxidation of β-diketones $RC(O)CH_2\cdot C(O)R'$ with *tert*-butyl hydroperoxide in the presence of $(acac)_2VO$, (PhH, 20°C, mol per mole of diketone)[a]

| Product | R = R′ = Me; 15 : 60 : 1[b] | R = Ph, R′ = Me; 10 : 50 : 1[b] | R = R′ = Ph; 10 : 50 : 1[b] |
|---|---|---|---|
| $CO_2$ | 0.86 | 0.70 | 0. 89 |
| *t*-BuOH | 3.40 | 4.36 | 4.68 |
| MeC(O)OBu-*t* | 0.03 | 0.04 | – |
| MeC(O)OOBu-*t* | 0.09 | 0.12 | – |
| PhC(O)OBu-*t* | – | 0.04 | 0.04 |
| PhC(O)OOBu-*t* | – | 0.14 | 0.06 |
| MeC(O)OH | 1.39[c] | 0.74 | – |
| PhC(O)OH | – | 0.69 | 1.74 |

[a] Averaged data.

[b] Ratio $RC(O)CH_2C(O)R'$–*t*-BuOOH–$(acac)_2VO$.

[c] Pyruvic acid was also detected qualitatively (as 2,4-dinitrophenylhydrazone); after treatment with diazomethane, methyl pyruvate was detected.

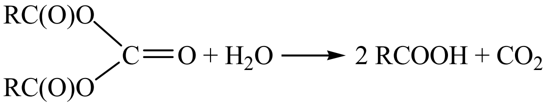
**Table 2.** Products of oxidation of 1,5-diphenylpentane-1,3,5-trione with *tert*-butyl hydroperoxide in the presence of (*acac*)$_2$VO (molar ratio 10 : 100 : 1, PhH, 20°C, mol per mole of the triketone)

| Product | Yield[a] |
|---|---|
| $CO_2$ | 1.80 |
| *t*-BuOH | 8.78 |
| $PhCOCH_3$ | 0.53 |
| PhC(O)OBu-*t* | 0.16 |
| PhC(O)OOBu-*t* | 0.14 |
| PhC(O)$CH_2$COOBu-*t* | 0.08 |
| PhC(O)OH | 1.14 |

[a] Averaged data.

methyl esters by IR spectroscopy. As follows from the data in Table 1, the yields of esters and peroxy esters are considerably lower than the yields of carboxylic acids, which suggests alternative way of their formation. Presumably, this alternative way is hydrolysis of anhydrides and diacyl carbonates (Scheme 4).

**Scheme 4.**

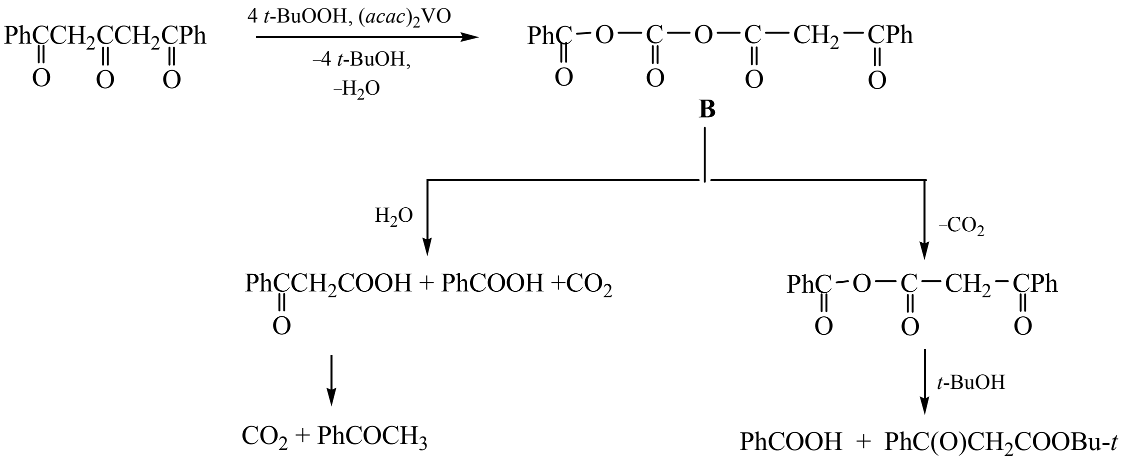


This fact confirms the formation of water in the oxidation of diketones to triketones (Scheme 1). In the oxidation of triketone **VI**, apart from carbon dioxide and benzoic acid, acetophenone was isolated as one of the main products (Table 2); it can be formed as a result of decarboxylation of benzoylacetic acid. The above compounds (Table 2) may be formed via oxidation of one methylene group in triketone **VI** according to Schemes 1–3 and subsequent transformations of diacyl carbonate **B** (Scheme 5).

*tert*-Butyl benzoylacetate was identified among the products, whereas neither free benzoylacetic acid nor its methyl ester was detected. This means that benzoylacetic acid is completely converted into acetophenone. However, in keeping with the data given in Table 2, the major oxidation product of 1,5-diphenylpentane-1,3,5-trione (**VI**) is benzoic acid. Moreover, the yield of carbon dioxide approaches 2 mol per mole of the substrate. Therefore, apart from processes described by Scheme 5, triketone **VI** is oxidized at the second methylene group, which leads to almost complete decomposition of the substrate. Benzoic anhydride thus formed gives rise to benzoic and peroxybenzoic acid esters.

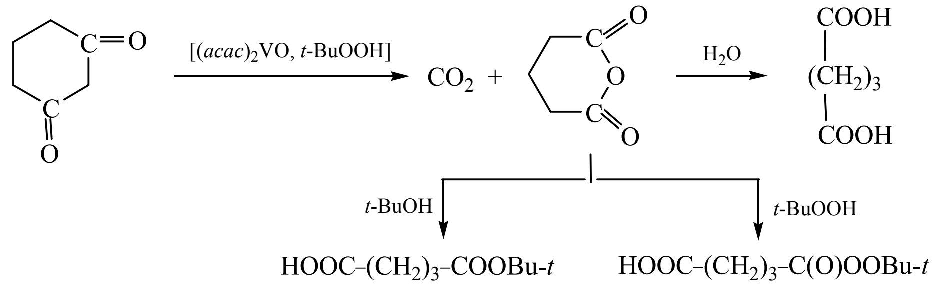
As noted above, cyclohexane-1,3-dione is oxidized with hydroperoxide **II** most readily in the presence of complex **I**. It is known that cyclohexane-1,3-dione exists preferentially in the enol form. At a substrate–*t*-BuOOH–(*acac*)$_2$VO ratio of 10 : 40 : 1 ($C_6H_6$, 20°C) we isolated 0.87 equiv of $CO_2$ and 3.41 equiv of *t*-BuOH. The titration of the reaction solution with 0.1 N NaOH revealed 1.62 equiv of carboxy groups, i.e., carboxylic acids are the major products. By analogy with acyclic β-diketones (Schemes 1–4) we presumed formation of pentanedioic acid as the major product, as well as its *tert*-butyl ester and monoperoxy ester.

**Scheme 5.**



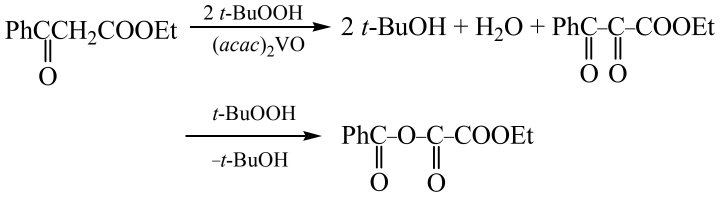
After treatment of the reaction solution with diazomethane, we identified dimethyl pentanedioate and methyl *tert*-butyl pentanedioate (0.26 and 0.05 equiv, respectively). We have synthesized an authentic sample of *tert*-butyl monoperoxypentanedioate, but this compound was not detected among the oxidation products. The overall yield of pentanedioic acid and its ester did not exceed 30%, indicating that the contribution of the reaction of the ketone form of cyclohexane-1,3-dione is not larger than 30%. However, the high yield of $CO_2$ suggests cleavage of the cyclohexane ring. Apart from the above products, acetaldehyde, ethyl acetate, methyl 2-methylbutanoate, and methyl 5-oxotetrahydrofuran-2-carboxylate were identified on a qualitative level, and other unidentified compounds were detected. These findings indicate that the oxidation of diketone **VII** involves methylene groups in the ring (Scheme 6).

**Scheme 6.**



Analogous processes involving oxidation of methylene group are typical of functionally substituted derivatives having an oxo group in the β-position. We examined the reaction of ethyl benzoylacetate (**VIII**) with hydroperoxide **II** in the presence of vanadium complex **I** (reactant molar ratio 10 : 40 : 1). In all cases the products were benzoic acid, carbon dioxide, and ethyl hydrogen oxalate. The amounts of the oxidation products almost did not change upon variation of the amount of the oxidant. The following products were identified at a reactant ratio of 10 : 40 : 1, mol per mole of **VIII**: *t*-BuOH, 3.70; ethanol, 0.07; $CO_2$, 0.26; benzoic acid, 0.30; ethyl oxalate, 0.13; *tert*-butyl benzoate, 0.02; *tert*-butyl peroxybenzoate, 0.02. The formation of these compounds may be rationalized assuming oxidation of the methylene group in ethyl benzoylacetate to give 3-phenyl-2,3-dioxopropionic acid ester and mixed benzoic 2-ethoxy-2-oxoacetic anhydride (Scheme 7).

**Scheme 7.**



$$\mathrm{Ph\underset{\underset{O}{\|}}{C}CH_2COOEt} \xrightarrow[(acac)_2\mathrm{VO}]{2\ t\text{-BuOOH}} 2\ t\text{-BuOH} + \mathrm{H_2O} + \mathrm{Ph\underset{\underset{O}{\|}}{C}\text{–}\underset{\underset{O}{\|}}{C}\text{–}COOEt}$$

$$\xrightarrow[-t\text{-BuOH}]{t\text{-BuOOH}} \mathrm{Ph\underset{\underset{O}{\|}}{C}\text{–}O\text{–}\underset{\underset{O}{\|}}{C}\text{–}COOEt}$$

We failed to isolate 3-phenyl-2,3-dioxopropionic acid ester, but its formation followed from the IR data. The IR spectrum of the nonvolatile residue, recorded in the region 750–1750 cm$^{-1}$, contained all absorption bands intrinsic to the initial ester, but bands belonging to stretching vibrations of the C(O)–O–C bonds (1146–1265 cm$^{-1}$) were broadened, and their resolution was impaired. In the region corresponding to carbonyl stretching vibrations we observed two doublets at 1687/1682 (PhCO) and 1737/1733 cm$^{-1}$ [C(O)OR]. The first of these belongs to ester **VIII**, and the other bands together with the band at 1712 cm$^{-1}$ (C=O, ketone) may be assigned to ethyl 3-phenyl-2,3-dioxopropionate.

The formation of mixed anhydride was confirmed by the identification of *tert*-butyl benzoate and *tert*-butyl peroxybenzoate. Hydrolysis of that anhydride yields benzoic acid and ethyl hydrogen oxalate. The latter undergoes partial oxidation to carbon dioxide and ethanol (Scheme 8).

**Scheme 8.**

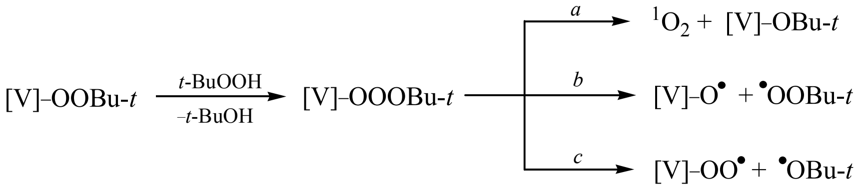
$$\mathrm{HO(O)C{-}C(O)OEt} \xrightarrow[-t\text{-BuOH}]{t\text{-BuOOH}} \left[\mathrm{HO(O)COC(O)OEt}\right] \longrightarrow 2\,\mathrm{CO_2} + \mathrm{EtOH}$$

Unlike β-diketones whose complete conversion may be attained by choosing an appropriate *t*-BuOOH–substrate ratio, up to 40% of initial ethyl benzoylacetate remains unchanged even in the presence of 6 equiv of the oxidant. The latter is consumed almost completely, but up to 30% of its amount is reduced to *t*-BuOH and $O_2$.

With a view to elucidate the nature of oxidant for the methylene group in β-dicarbonyl compounds we used diketone **V** as model compound. Compound **V** did not react with hydroperoxide **II** at a molar ratio of 1:5 (benzene, 20°C, 20 h). We examined oxidation of 1,3-diphenylpropane-1,3-dione (**V**) with *tert*-butyl hydroperoxide in the presence of vanadyl acetylacetonate (**I**), as well as the reaction of **V** with the system V(OBu-*t*)$_4$–*t*-BuOOH (molar ratio 1:1:6, benzene, 20°C). Among the oxidation products we identified (mol per mole of **V**): *t*-BuOH, 7.50; $CO_2$, 0.90; benzoic acid, 1.60; *tert*-butyl benzoate, 0.03; *tert*-butyl peroxybenzoate, 0.07. The products isolated in the reactions with vanadyl acetylacetonate and vanadium tetra-*tert*-butoxide were identical, which suggests common mechanism of their formation.

The reaction of (*t*-BuO)$_4$V [10] and (*acac*)$_2$VO [6] with *tert*-butyl hydroperoxide (**II**) includes the formation of vanadium-containing peroxides and trioxides. The latter decompose both with liberation of singlet oxygen and homolytically (Scheme 9).

**Scheme 9.**

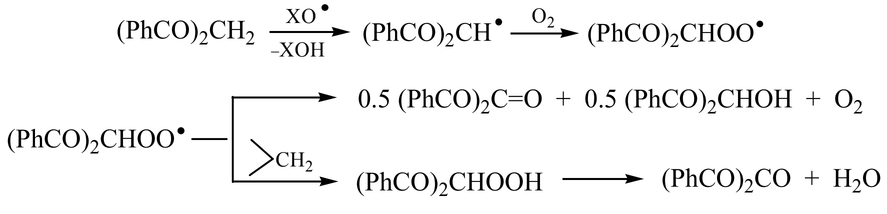


In the presence of oxygen-centered radical species singlet oxygen is converted into triplet [11]. Oxidation of C–H bonds in the system (*t*-BuO)$_4$V–*t*-BuOOH with oxygen (Scheme 9, path *a*) is initiated by oxygen-centered radicals and follows homolytic pattern [10]. Taking into account published data and our results, we presumed that in the reactions under study methylene group is oxidized to carbonyl by the action of oxygen generated by reaction of (*acac*)$_2$VO with *t*-BuOOH [6]. The formation of trioxo derivatives may be illustrated by Scheme 10.

Dibenzoylmethanol should be transformed into ketone, for the system (*acac*)$_2$VO–*t*-BuOOH is known to be one of the best oxidants for secondary alcohols [12].

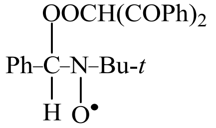
Homolytic character of the oxidation of methylene group is confirmed by the ESR data. The oxidation of dibenzoylmethane $(PhCO)_2CH_2$ with vanadyl acetylacetonate (**I**)–*t*-BuOOH and (*t*-BuO)$_4$V–*t*-BuOOH was studied by ESR spectroscopy in the presence of *N*-benzylidene-*tert*-butylamine *N*-oxide (*C*-phenyl-*N*-*tert*-butylnitrone, (PBN) as spin trap. In both cases, the ESR spectra were identical: they were a triplet of doublets with hyperfine coupling constants $a_i(^{15}N)$ = 1.32 mT, $a_i$(H) = 0.152 mT, $g_i$ = 2.0060 (see figure). In the case of (*t*-BuO)$_4$V the signal appeared immediately

**Scheme 10.**



X = [V]–OO•; *t*-BuOO•; [V]–O•; *t*-BuO•.

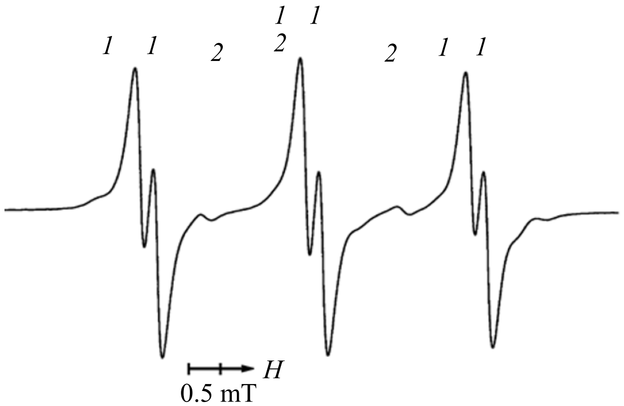
after mixing of the reactants, whereas in the reaction with $(acac)_2VO$, the signal appeared in 25 min. After 1 h, its intensity increased, indicating its generation with time. Insofar as the observed hyperfine coupling constants differed from those typical of PBN adducts with *tert*-butylperoxy radicals [13, 14] and $V(O)OO^{\cdot}$ [10], we believe that the spectrum belongs to the adduct of PBN with peroxy radical derived from the substrate. After some time, a minor triplet signal (1 : 1 : 1) appeared, whose isotropic parameters [$g_i$ = 2.0069, $a_i(^{15}N)$ = 0.790 mT] corresponded to benzoyl-*tert*-butylnitroxyl radical $PhC(O)N(O^{\cdot})Bu$-*t*. The latter was formed as a result of oxidation of PBN with singlet oxygen or peroxy radicals [15].



$$\begin{array}{c} OOCH(COPh)_2 \\ | \\ Ph\text{–}C\text{–}N\text{–}Bu\text{-}t \\ |\quad | \\ H\quad O^{\bullet} \end{array}$$

Apart from Scheme 10 proposed for the oxidation of methylene group, nucleophilic addition of *tert*-butyl hydroperoxide or vanadium-containing peroxy compound at the carbonyl group of the substrate and subsequent transformation into triketone [6] cannot be ruled out. With a view to verify whether the latter path is possible diketone **V** was brought into reaction with *N*-(2-oxidophenyl)salicylideneaminato(*tert*-butylperoxo)-vanadyl (**IX**) (1:2, methylene chloride, 20°C). It is known that peroxy compounds of this type act as hydroxylating agents toward aliphatic and aromatic compounds [16]. In the reaction of peroxide **IX** with diketone **V** (2 days) we isolated 0.72 equiv of $CO_2$ and 0.56 equiv of benzoic acid, whereas neither benzoic nor peroxybenzoic acid ester was detected. The process was fairly complicated; the oxidation was likely to be accompanied by decomposition of the peroxide and formation of tarry products that were insoluble in diethyl ether and arenes; therefore, we failed to perform complete qualitative analysis of the products. No signals were observed in the ESR spectra both in the absence and in the presence of spin traps [*tert*-butylnitrone, *C*-phenyl-*N*-*tert*-butylnitrone]. Thus the results of the reaction of dibenzoylmethane with peroxide **IX** indicated that vanadium-containing peroxy compounds can participate in the oxidation of C–H bond, but this reaction direction is minor.

Free oxygen (~20%, calculated on the initial amount of the hydroperoxide) was detected in addition to the oxidation products of diketone **V** given in Table 1. Liberation of oxygen was also observed in the reaction with vanadium tetra-*tert*-butoxide. Therefore, the amount of hydroperoxide necessary for complete conversion of β-diketone always exceeds its stoichiometric amount. Incomplete conversion of ethyl benzoylacetate may be rationalized in terms of competition between generation of oxygen and oxidation of the methylene group in the substrate.



ESR spectrum of $(PhCO)_2CH_2$–*t*-BuOOH–$(acac)_2VO$ (1 : 5 : 0.1) in benzene in the presence of PBN, recorded at 20°C in 20 min after mixing the reactants (degassed sample): (*1*) $(PhCO)_2CHOOCH(Ph)N(Bu\text{-}t)O^{\cdot}$, (*2*) $PhC(O)N(Bu\text{-}t)O^{\cdot}$.

It should be noted that systems based on *t*-BuOOH and chromium(III) and cobalt(II) acetylacetonates, which also generate oxygen, do not oxidize 1,3-diphenylpropane-1,3-dione. Coordinately unsaturated $(acac)_2Co$ is likely to form a complex with diketone **V**, resulting in sharp deceleration of the reaction between components of the oxidizing system.

We can conclude that *tert*-butyl hydroperoxide in the presence of vanadyl acetylacetonate (**I**) is an effect-tive oxidant toward β-dicarbonyl compounds. The oxidation process involves the decomposition of the substrate carbon skeleton, the formation of carboxylic acids, and the liberation of carbon dioxide. Complex **I** catalyzes these reactions. Oxidation of methylene group to carbonyl with the formation of trioxo com-pounds follows mainly homolytic pattern according to Schemes 9 and 10. The subsequent nucleophilic reaction of trioxo compounds with *tert*-butyl hydroperoxide or vanadium-containing peroxides leads to oxidative cleavage of carbon–carbon bonds, yielding final products through the corresponding carboxylic acid anhydrides.

## EXPERIMENTAL

The IR spectra were recorded in KBr or from thin films on an IR-Prestige-21 spectrometer. The ESR spectra were obtained on a Bruker ER-200D-SRC spectrometer equipped with an ER 4105DR double resonator (operating frequency ~9.5 GHz) and ER 4111VT temperature control unit. Diphenylpicrylhydrazyl (DPPH) was used as reference for the determination of *g* factor. Analysis was performed in the probe of the ESR spectrometer. The reaction solutions were preliminarily degassed to improve resolution and remove oxygen generated by reaction of compounds **I** and **II**. The concentration of vanadyl acetylacetonate (**I**) did not exceed 0.005 M.

Chromatographic analysis of liquid products was performed on a Tsvet-160 chromatograph equipped with a flame ionization detector; carrier gas argon; sorbent Chromaton N-AW-DMCS. Volatile components (*tert*-butyl alcohol, ethanol, pentane-2,4-dione, methyl acetate) were analyzed using a 2400 × 3-mm column packed with 10% of poly(ethylene glycol) adipate on TZKM fire-brick, oven temperature 50–80°C). *tert*-Butyl acetate and *tert*-butyl peroxyacetate were analyzed using a 3000 × 3-mm column; stationary phase 5% SP-2401, oven temperature 50°C. Carboxylic acid ester (methyl benzoate, *tert*-butyl benzoate, isopropyl benzoate, ethyl methyl oxalate), acetophenone, etc. were identified on a 1200 × 3-mm column; stationary phase 15% of Apiezon, oven temperature 135–150°C. Ethyl benzoyl acetate was determined using a 1200 × 3-mm column packed with 5% of OV-17 on Inerton Super; oven temperature 165–170°C. The components were quantitated by the external standard technique using authentic samples in each case.

The amount of aliphatic acids in nonvolatile residues was determined according to the procedure described in [17]. Carboxylic acids were identified as methyl esters after treatment with diazomethane. Quantitative analysis of hydroperoxides was performed by iodometric titration. Carbonyl compounds were identified as 2,4-dinitrophenylhydrazones by the melting point and by TLC using authentic samples [Silpearl, Silufol UV-254; benzene or benzene–diethyl ether (18 : 1)]. The amount of liberated oxygen was determined by the weight of benzoic acid formed by reaction of oxygen with benzaldehyde [18]. In order to determined the amount of carbon dioxide, the oxidation of β-diketones was carried out in a two-necked flask equipped with a reflux condenser. The latter was connected sequentially to two gas-washing bottles charged with a saturated solution of $Ba(OH)_2$. The system was preliminarily evacuated and filled with argon. The flask was charged with a mixture of reactants, and argon was passed periodically through the mixture until barium carbonate no longer separated. The precipitate of $BaCO_3$ was filtered through a glass frit and dried at 100°C until constant weight.

Vanadyl acetylacetonate (**I**) was synthesized from $V_2O_5$ via successive treatment with freshly distilled acetylacetone and with a solution of sodium carbonate [19]; mp 252°C [20]. Pentane-2,3,4-trione was prepared by oxidation of pentane-2,4-dione with *p*-nitroso-*N*,*N*-dimethylaniline; bp 55–57°C (12 mm) [21]. Vanadium tetra-*tert*-butoxide was synthesized by exchange reaction of vanadium trichloride and lithium *tert*-butoxide at a ratio of 1 : 2 in hexane, followed by heating for 2 h under reflux. Removal of the solvent and subsequent vacuum distillation gave $V(OBu\text{-}t)_4$ as a dark blue liquid, which was very sensitive to atmospheric oxygen and moisture; bp 89–90°C (1 mm) [22]. *N*-(2-Oxidophenyl)salicylideneaminato(*tert*-butylperoxo)vanadyl was obtained by successive treatment of $(i\text{-PrO})_3VO$ with *N*-salicylidene-2-aminophenol and *tert*-butyl hydroperoxide [23]; the complex was isolated as dark brown crystals which were stable at 2–10°C; its activity was 99%. Found: $O_{act}$ 4.29%. $C_{17}H_{18}NO_5V$. Calculated: $O_{act}$ 4.36%. The IR spectrum of the complex was identical to that reported previously. The concentration of *tert*-butyl hydroperoxide was no less than 99.6–99.8%. The following commercial reagents were used: 1-phenylbutane-1,3-dione (98%, Acros Organics), 1,5-diphenylpentane-1,3,5-trione (≥98%, Fluka), 1-phenylbutane-1,3-dione (>98%, Fluka), ethyl benzoylacetate (95%, Fluka), cyclohexane-1,3-dione (97%, Alfa Aesar).

**Oxidation of pentane-2,4-dione with $(acac)_2VO$–*t*-BuOOH (15 : 1 : 60) in benzene.** A flask was charged with 0.04 g of vanadyl acetylacetonate (**I**), 0.24 g of acetylacetone, and 0.86 g of *t*-BuOOH in 20 ml of benzene. After 15 min, the mixture spontaneously warmed up, and evolution of $CO_2$ started. After 14 h, the amount of $BaCO_3$ was 0.42 g (0.09 g of $CO_2$). The solvent was distilled into a trap cooled with liquid nitrogen. Chromatographic analysis of the distillate showed the presence of 0.57 g of *t*-BuOH, 0.002 g of *tert*-butyl peroxyacetate, and 0.01 g of *tert*-butyl acetate and, after treatment with diazomethane, 0.23 g of methyl acetate. The amount of acetic acid (0.19 g) was also confirmed by titration of the distillate with a 0.1 N solution of NaOH. According to the TLC data, the volatile products before and after treatment with diazomethane contained pyruvic acid and its methyl ester (identified as the corresponding 2,4-dinitrophenylhydrazones).

**Reaction of 1,3-diphenylpropane-1,3-dione with (*acac*)$_2$VO–*t*-BuOOH (10 : 1 : 50).** A flask was charged with 0.034 g of (*acac*)$_2$VO, 0.28 g of diketone **V**, and 0.56 g of *tert*-butyl hydroperoxide in 12 ml of benzene (20°C). After 20 h, the originally violet–red transparent solution turned red–brown, and no solid separated. The amount of $BaCO_3$ was 0.22 g (0.049 g of $CO_2$). The solvent was recondensed into a trap; the condensate contained 0.43 g of *tert*-butyl alcohol and 0.01 g of *tert*-butyl benzoate (according to the GLC data).

In a parallel run, the concentrations of *tert*-butyl peroxybenzoate and benzoic acid in the reaction solution were determined before removal of volatile products. The amount of *tert*-butyl peroxybenzoate was determined by reaction with ($i$-PrO)$_3$Al [24]. For this purpose, a sample of the reaction mixture was treated with excess aluminum triisopropoxide, and the resulting mixture was heated for 10 h at 70°C in a sealed ampule. By chromatography we determined 0.01 g of isopropyl benzoate, which corresponds to 0.012 g of *tert*-butyl peroxybenzoate. Acetone was identified by TLC as 2,4-dinitrophenylhydrazone.

Benzoic acid was determined as follows. A part of the reaction solution was treated with 10% sulfuric acid, the organic phase was separated, and the aqueous acid layer was thoroughly extracted with diethyl ether. The extracts were combined with the organic phase, dried over $Na_2SO_4$, and treated with diazomethane. The amount of methyl benzoate was 0.28 g.

The reaction was also accompanied by liberation of oxygen which was determined according to the procedure described in [18]. The reaction was carried out in an H-shaped ampule, one arm of which was charged with 0.2 ml of benzaldehyde, and the other, with 0.013 g of (*acac*)$_2$VO, 0.22 g of *tert*-butylhydroperoxide, and 0.11 g of 1,3-diphenylpropane-1,3-dione in 5 ml of benzene. The contents of both arms were frozen, and the ampule was degassed and sealed. Evolution of oxygen was observed upon defrosting, and the reaction solution turned cherry red. After 2 days, the ampule with benzoic acid was sealed off, and excess benzaldehyde was removed. The amount of benzoic acid was determined by weighing, as well as by titration with a 0.1 N solution of sodium hydroxide in the presence of phenolphthalein. The amount of benzoic acid was 0.08 g, which corresponded to 0.010 g of oxygen.

**Reaction of 1,5-diphenylpentane-1,3,5-trione with (*acac*)$_2$VO–*t*-BuOOH (10 : 1 : 100).** Triketone **VI**, 0.33 g, was added to 0.033 g of (*acac*)$_2$VO in 15 ml of benzene. The originally greenish–blue solution turned dark green in a few minutes, indicating formation of a vanadyl complex with triketone **VI**. *tert*-Butyl hydroperoxide, 1.13 g, was then added, and the solution immediately turned wine red due to formation of either vanadium complexes with hydroperoxide or vanadium peroxo compounds. The reaction mixture was kept for 20 h. During that time, the main amount of carbon dioxide liberated. When the liberation of $CO_2$ was complete, the solution became transparent and orange–red. We isolated 0.38 g of $BaCO_3$ (0.084 g of $CO_2$). According to the GLC data, the reaction solution contained 0.78 g of *t*-BuOH, 0.075 g of acetophenone, 0.034 g of *tert*-butyl benzoate, and 0.022 g of *tert*-butyl benzoylacetate. *tert*-Butyl benzoylacetate was identified by IR spectroscopy, and its amount was determined by chromatography (by ethyl benzoylacetate). Treatment of a part of the reaction solution with 2,4-dinitrophenylhydrazine gave acetophenone 2,4-dinitrophenylhydrazone, mp 246–247°C (the same for mixed sample). Treatment of a sample withdrawn from the solution with aluminum triisopropoxide gave 0.03 g of isopropyl benzoate, which corresponds to 0.038 g of *tert*-butyl peroxybenzoate. The amount of benzoic acid (0.17 g) was determined from the weight of methyl benzoate (0.194 g) obtained by treatment of the reaction solution with diazomethane. Benzoylformic acid (a possible dibenzoylacetone oxidation products) was not detected as methyl ester.

In a special experiment, when evolution of carbon dioxide terminated, benzene and volatile products were condensed in a trap cooled with liquid nitrogen. The residue was a thick greenish–brown material including white crystals. It was hydrolyzed with a 10% solution of sulfuric acid and extracted with freshly distilled diethyl ether. The amount of *tert*-butyl peroxybenzoate in the extract was determined by iodometric titration in the presence of $Fe^{2+}$.

**Oxidation of ethyl benzoylacetate with (*acac*)$_2$VO–*t*-BuOOH (10 : 1 : 60).** The reaction mixture consisted of 0.033 g of (*acac*)$_2$VO, 0.25 g of ester **VIII**, and 0.71 g of *t*-BuOOH in 10 ml of benzene. After 20 min, the originally crimson solution turned red, and after 1 h, orange. We isolated 0.066 g of $BaCO_3$. The reaction solution contained 0.47 g of *t*-BuOH, 0.004 g of ethanol, 0.005 g of *tert*-butyl benzoate, 0.007 g of *tert*-butyl peroxybenzoate, and 0.105 g of unreacted ester **VIII**.

After treatment with diazomethane, 0.042 g of methyl benzoate (0.038 g of PhCOOH) and 0.02 g of ethyl methyl oxalate (0.018 g of ethyl hydrogen oxalate) were determined. When the benzene solution was kept for about 2 days at room temperature, it turned light yellow. A blue solid separated at the bottom of the flask; in keeping with published data, it was vanadium(IV) oxide.

The reactions of 1-phenylbutane-1,3-dione and cyclohexane-1,3-dione with *tert*-butyl hydroperoxide in the presence of $(acac)_2VO$, as well as the oxidation with $(t\text{-BuO})_4V$–$t$-BuOOH, were carried out in a similar way, and the products were analyzed as described above. In the oxidation of benzoylacetone, acetic and benzoic acids in the condensed volatile fraction and in the hydrolyzate of nonvolatile residue, respectively, were analyzed as methyl esters after treatment with diazomethane. The amounts of *tert*-butyl peroxyacetate and *tert*-butyl peroxybenzoate were determined from the amounts of the corresponding isopropyl esters and acetone after treatment of the reaction solution with aluminum triisopropoxide.

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