Peroxidation of β-diketones and β-keto esters with *tert*-butyl hydroperoxide in the presence of $Cu(ClO_4)_2/SiO_2$*

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Reactions of β-diketones and β-keto esters with *tert*-butyl hydroperoxide under heterogeneous conditions using SiO_2-supported copper(II) perchlorate as a catalyst give rise to α-peroxidation products in 65—82% yields. A possibility to reuse the catalyst was demonstrated.

Key words: peroxides, *tert*-butyl hydroperoxide, β-diketones, β-keto esters, copper compounds, silica gel.

For more than half a century, organic peroxides have been used in industry as initiators of radical polymerization and cross-linkage. Their assortment includes dialkyl peroxides, diacyl peroxides, peroxy esters, peroxy dicarbonates, peroxy carbonates, peroxy acetals, cyclic triperoxides, and terminal bishydroperoxides.[1,2] In the last decades, these compounds were found to possess antimalarial,[3] antihelmintic,[4] and antitumor activity.[5] Peroxides are of interest as potential explosives.[6]

The interest to the preparation of efficient inexpensive initiators of radical polymerization and biologically active compounds stimulates the development of new methods for the synthesis of peroxides, mostly from ketones and their derivatives reacted with hydrogen peroxide and hydroperoxides.[7]

In the present work, we continue our studies on the peroxidation of dicarbonyl compounds.[8] Earlier, it was found that Cu, Fe, Mn, and Co compounds catalyze selective α-peroxidation of β-dicarbonyl compounds with *tert*-butyl hydroperoxide.[8a,b]

Transition metals such as Cu, Mn, and Co in combination with hydroperoxides have been used for the first time by Kharasch for the preparation of peroxides from alkenes, ketones, and tertiary amines more than 60 years ago.[9] Afterwards, the formation of peroxides was observed in the reactions of hydroperoxides in the presence of metal salts (copper,[10] cobalt,[11] and iron[12,13]) or their complexes (nickel complexes,[14] palladium acetate,[15] and ruthenium bipyridinate on montmorillonite[16]). Peroxides were obtained in good yields by peroxidation of amines, amides, and lactams catalyzed by ruthenium salts.[17] Formation of peroxides was observed in the oxidation of cyclic β-diketones with a singlet oxygen,[18] the $CeCl_3/O_2$ system,[19] as well as in the oxidation of nitrogen-containing heterocycles upon treatment with manganese salts and oxygen.[20] It is important to note that virtually all the studies on peroxidation were carried out under homogeneous conditions because of the tendency of peroxides to decompose on a solid surface under heterogeneous conditions.[21]

The above-mentioned reactions for the preparation of peroxides which use salts of metals of variable oxidation state are rather exceptions from the practice of peroxide chemistry, since they are applicable only to compounds of a certain structure, whereas the overwhelming majority of peroxide transformations in the presence of metal salts includes the cleavage of the O—O bond.[22]

In the present work, we accomplished the peroxidation of β-dicarbonyl compounds at α-position with *tert*-butyl hydroperoxide under heterogeneous conditions using copper(II) perchlorate hexahydrate supported on silica gel as a catalyst.

Results and Discussion

In our studies, monosubstituted at α-position β-diketones **1a—e** and β-keto esters **1f—i** (Scheme 1) served as the starting reactants.

Field emission scanning electron microscopy (FE-SEM) studies of the samples of the starting silica gel and the catalyst prepared on its basis (20% wt.% of $Cu(ClO_4)_2$ on SiO_2) showed that the structure of the sample slightly changes after the treatment. A commercial sample contains small particles of silica gel on the surface of larger grains (Fig. 1, *a*). In the sample of silica gel with

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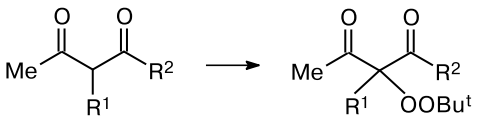
Scheme 1



Compounds **1**, **2**	R^1	R^2
a	*n*-C_6H_{13}	Me
b	CH_2=$CHCH_2$	Me
c	CH_2CH_2COOEt	Me
d	Bn	Me
e	4-$MeC_6H_4CH_2$	Me
f	Me	OEt
g	Bu	OEt
h	CH_2CH_2CN	OEt
i	Bn	OEt

Conditions: Bu^tOOH, $Cu(ClO_4)_2/SiO_2$, solvent.

supported copper(II) perchlorate, the amount of small particles on the surface of large grains considerably increases (Fig. 1, *b*). The X-ray microanalysis showed that the catalyst is uniformly distributed over the surface of silica gel. The concentration of copper and chlorine atoms measured upon scanning along an arbitrary chosen lines on the surface of the sample did not change.

The search for optimal conditions was performed using α-benzylacetylacetone **1d** as a model compound (see Table 1, entries *4—11*).

The product **2d** was obtained in acceptable yield with the v/v ratio $CHCl_3$: MeCN ranging from 4 : 1 to 20 : 1 (Table 1, entries *4—9*). Virtually no peroxide **2d** was formed for the ratio $CHCl_3$: MeCN = 100 : 1 (entry *10*). The formation of **2d** was not observed either when pure chloroform, 1,2-dichloroethane, or toluene were used (entry *11*), that can be apparently explained by low solubility of $Cu(ClO_4)_2$ in these solvents.

A possibility of the catalyst reuse was shown for the model synthesis of peroxide **2d** in the $CHCl_3$—MeCN (10 : 1) solvent system, in which the solubility of $Cu(ClO_4)_2$ is insignificant (Table 2).

Good yields of peroxidation product **2d** were achieved in the first three cycles of the catalyst reuse, whereas in subsequent cycles they were considerably lower. In all the experiments, the $Cu(ClO_4)_2 \cdot 6H_2O/SiO_2$ catalyst mass loss as a result of partial dissolution of copper perchlorate and losses during regeneration was insignificant, about 3—5% after each cycle.

Other peroxides **2a—c** and **2e—i** were synthesized under conditions described in entry *6* (see Table 1). The peroxidation of β-keto esters **1f—i** required a larger amount of the catalyst. Using compound **1e** as an example, we showed a possibility of a five-fold scaling of the synthesis (entry *12*). The catalyst reuse was also tested in the case of substrate **1h** (entry *15*).

In conclusion, a suggested method for the α-peroxidation of β-diketones and β-keto esters can be used for the structurally different starting compounds. In all the experiments, the product yields ranges within 65—82%, that allows one to extend this procedure to other dicarbonyl compounds. Despite heterogeneous conditions of the process, no noticeable decomposition of the peroxide products and *tert*-butyl hydroperoxide occurs. The catalyst can be regenerated and efficiently enough used in three consecutive cycles.

Experimental

^1H NMR spectra were recorded on a Bruker AM 300 spectrometer (300.13 MHz for ^1H, 75.48 MHz for ^{13}C) in $CDCl_3$. To perform scanning electronic microscopy,[23] the samples before studies were placed on the surface of aluminum stage 25 mm in diameter and fixed by a conducting glue. A 10 nm conducting layer of metal (Pt/Pd, 80/20) was applied on the samples using magnetron sputtering. The microstructures of the samples were studied by field emission scanning electron microscopy

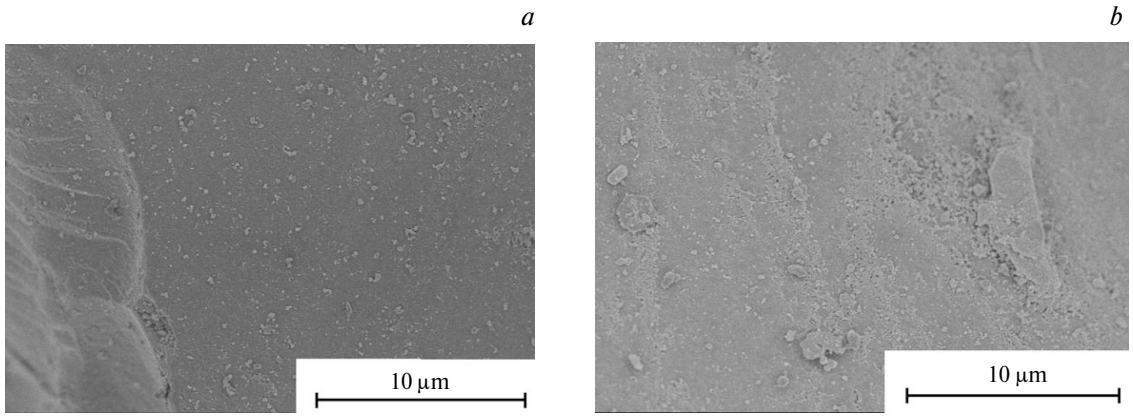


Fig. 1. Microphotographs of the samples of commercial SiO_2 (*a*) and the catalyst $Cu(ClO_4)_2 \cdot 6H_2O/SiO_2$ (*b*).

Table 1. Peroxidation of β-dicarbonyl compounds **1a—i** with *tert*-butyl hydroperoxide[a]

Entry	Starting compound	Method of stirring[b]	Solvent	Product	Product yield[c] (%)
1	**1a**	MS	$CHCl_3$—MeCN (10 : 1)	**2a**	68
2	**1b**	MS	$CHCl_3$—MeCN (10 : 1)	**2b**	65
3	**1c**	MS	$CHCl_3$—MeCN (10 : 1)	**2c**	72
4	**1d**	MS	$CHCl_3$—MeCN (4 : 1)	**2d**	79
5	**1d**	US	$CHCl_3$—MeCN (4 : 1)	**2d**	80
6	**1d**	MS	$CHCl_3$—MeCN (10 : 1)	**2d**	73
7	**1d**	US	$CHCl_3$—MeCN (10 : 1)	**2d**	75
8	**1d**	MS	$CHCl_3$—MeCN (20 : 1)	**2d**	65
9	**1d**	US	$CHCl_3$—MeCN (20 : 1)	**2d**	59
10	**1d**	MS	$CHCl_3$—MeCN (100 : 1)	**2d**	—[d]
11	**1d**	MS	$CHCl_3$[e]	**2d**	—[d]
12	**1e**	MS	$CHCl_3$—MeCN (10 : 1)	**2e**	75 (73)[f]
13	**1f**	MS	$CHCl_3$—MeCN (10 : 1)	**2f**	75
14	**1g**	MS	$CHCl_3$—MeCN (10 : 1)	**2g**	71
15	**1h**	MS	$CHCl_3$—MeCN (10 : 1)	**2h**	72 (67, 61)[g]
16	**1i**	MS	$CHCl_3$—MeCN (10 : 1)	**2i**	82

[a] Conditions: 20 mol.% of [Cu] were used per 1 mol of the starting compound in the case of diketones **1a—e** or 40 mol.% of [Cu] in the case of keto esters **1f—i**, 6 mmol of Bu^tOOH, 7 mL of the solvent; reflux, 6 h.
[b] MS stands for mechanical stirring, US stands for sonication.
[c] Calculated on the isolated product.
[d] Trace amounts.
[e] The same result was obtained when 1,2-dichloroethane or toluene were used.
[f] Five-fold scaling of loading.
[g] For two reuses of the catalyst.

Table 2. The efficiency of the catalytic system $Cu(ClO_4)_2 \cdot 6H_2O/SiO_2$ in six catalytic cycles of the preparation of peroxide **2d**

Cycle	Amount of catalyst loaded in reaction/mg	Loss in weight of the catalyst[a] (%)	Yield of **2d**[b] (%)
1	687	—	73
2	667	3	71
3	646	3	68
4	627	3	55
5	596	5	43
6	572	4	33

[a] Based on the initial amount of the catalyst taken in the cycle.
[b] Yield of the isolated product.

(FE-SEM) on a Hitachi SU8000 electron microscope. The images were obtained in the mode of registration of secondary electrons at accelerating voltage of 10 kV and operating distance of 8—10 mm. The morphology of the samples was studied with the correction on the surface effects of the conducting layer sputtering.

Thin-layer chromatography was carried out on Silufol UV-254 plates with Silpearl sorbent in petroleum—ethyl acetate solvent systems. Commercially available reactants were purchased from Acros. Domestically produced solvents were distilled before use. Silica gel (0.060—0.200 mm, 60 Å, CAS 7631-86-9, Acros) was used for column chromatography and for the preparation of the $Cu(ClO_4)_2/SiO_2$ catalyst. Ultrasonic experiments were performed using a UZV-3/200-TN-RELTEK ultrasonic bath (290 W, 22 kHz).

Dicarbonyl compounds **1a**,[24] **1b**,[25] **1c**,[26] **1d**,[27] **1e**,[28] **1g**,[29] **1h**,[30] **1i**[31] were synthesized according to the known procedures.

3-Hexylpentane-2,4-dione (1a).[24] An oil. ^{1}H NMR, δ: 0.83 (t, 3 H, $C\underline{H}_3CH_2$, J = 6.6 Hz); 1.22—1.26 (m, 8 H); 1.78 (q, 1.5 H, $CHC\underline{H}_2$, J = 7.3 Hz); 2.02—2.17 (m, 6.5 H); 3.56 (t, 0.6 H, $C\underline{H}CH_2$, J = 7.3 Hz), 16.63 (br.s, 0.4 H, OH).

3-Allylpentane-2,4-dione (1b).[25] An oil. ^{1}H NMR, δ: 2.06 (s, 3 H, CH_3); 2.13 (s, 3 H, CH_3); 2.57 (m, 1 H, $CHC\underline{H}_2CH$); 2.95 (d, 1 H, $CHC\underline{H}_2C$, J = 5.1 Hz); 3.69 (t, 0.5 H, CHCO, J = 7.3 Hz); 4.93—5.86 (m, 3 H, $C\underline{H}_2C\underline{H}CH_2$); 16.67 (br.s, 0.5 H, OH).

Ethyl 4-acetyl-5-oxohexanoate (1c).[26] An oil. ^{1}H NMR, δ: 1.22 (t, 3 H, $C\underline{H}_3CH_2$, J = 6.9 Hz); 2.04—2.58 (m, 10 H, CH_3CO, 2 CH_2); 3.70 (t, 0.6 H, CH, J = 6.9 Hz); 4.06—4.13 (m, 2 H, CH_2O); 16.82 (br.s, 0.4 H, OH).

3-Benzylpentane-2,4-dione (1d).[27] An oil. ^{1}H NMR, δ: 2.07 (s, 3 H, CH_3); 2.12 (s, 3 H, CH_3); 3.15 (d, 1 H, $C\underline{H}_2CH$, J = 7.3 Hz); 3.65 (s, 1 H, CH_2); 4.00 (t, 0.7 H, CH, J = 7.3 Hz); 7.13—7.30 (m, 5 H, CH_{Ar}); 16.82 (br.s, 0.3 H, OH).

3-(4-Methylbenzyl)pentane-2,4-dione (1e).[28] An oil. ^{1}H NMR, δ: 2.06 (s, 3 H, CH_3); 2.11 (s, 6 H, CH_3); 2.30 (s, 1.5 H, CH_3C_{Ar}); 2.32 (s, 1.5 H, CH_3C_{Ar}); 3.10 (d, 1 H, $C\underline{H}_2CH$, J = 7.3 Hz); 3.61 (s, 1 H, CH_2); 3.99 (t, 0.5 H, CH, J = 7.3 Hz); 6.97—7.15 (m, 4 H, CH_{Ar}); 16.81—16.83 (br.s, 0.5 H, OH).

Ethyl 2-acetylhexanoate (1g).[29] A colorless oil. ^{1}H NMR, δ: 0.84 (t, 3 H, $C\underline{H}_3CH_2CH_2$, J = 6.6 Hz); 1.16—1.35 (m, 7 H,

$C\underline{H}_3CH_2O$, $C\underline{H}_2C\underline{H}_2$); 1.72—1.87 (m, 2 H, $C\underline{H}_2CH$); 2.17 (s, 3 H, CH_3CO); 3.33 (t, 1 H, CH, J = 7.3 Hz); 4.14 (q, 2 H, CH_2O, J = 7.3 Hz).

Ethyl 2-(2-cyanoethyl)-3-oxobutanoate (1h).[30] A colorless oil. ^{1}H NMR, δ: 1.25 (t, 3 H, $C\underline{H}_3CH_2O$, J = 6.9 Hz); 2.05—2.16 (m, 2 H, CH_2CH); 2.25 (s, 3 H, $C\underline{H}_3COCH$); 2.40 (t, 2 H, CH_2CN, J = 7.0 Hz); 3.60 (t, 1 H, CH, J = 6.9 Hz); 4.19 (q, 2 H, CH_2O, J = 7.0 Hz).

Ethyl 2-benzyl-3-oxobutanoate (1i).[31] A colorless oil. ^{1}H NMR, δ: 1.18 (t, 3 H, $C\underline{H}_3CH_2$, J = 7.3 Hz); 2.16 (s, 3 H, CH_3CO); 3.14 (d, 2 H, $C\underline{H}_2CH$, J = 8.1 Hz); 3.76 (t, 1 H, CH, J = 7.3 Hz); 4.13 (q, 2 H, CH_2O, J = 7.3 Hz); 7.14—7.27 (m, 5 H, CH_{Ar}).

A catalyst $Cu(ClO_4)_2 \cdot 6H_2O/SiO_2$. The salt $Cu(ClO_4)_2 \cdot 6H_2O$ (195 mg) was added to MeOH (5 mL) with stirring, after its complete dissolution SiO_2 (495 mg, 80 wt.% calculated on $Cu(ClO_4)_2$) was added. The mixture was treated with ultrasound for 10 min. The solvent was evaporated *in vacuo* of a water-jet pump at 60 °C for 20 min to obtain $Cu(ClO_4)_2 \cdot 6H_2O/SiO_2$ (687 mg) with the mass content of $Cu(ClO_4)_2$ about 20%. The catalyst with the content of $Cu(ClO_4)_2$ about 40% was obtained similarly, using SiO_2 (150 mg, 60 wt.% of SiO_2 calculated on $Cu(ClO_4)_2$.).

Peroxides 2a—e (general procedure). A catalyst $Cu(ClO_4)_2 \cdot 6H_2O/SiO_2$ (642—935 mg, 0.2 mol of [Cu] per 1 mol of the substrate) was added to a solution of diketone **1a—e** (500 mg, 2.45—3.57 mmol) in a proper solvent (7 mL), the mixture was brought to reflux and 70% aqueous Bu^{t}OOH (1.89—2.76 g, 14.7—21.4 mmol, 6 mol of Bu^{t}OOH per 1 mol of the substrate) was added in six portions (0.32—0.46 g each) every 1 h. After addition of the last portion, the mixture was refluxed for 1 h. The mixture was subjected to ultrasound or vigorous mechanical stirring using an upper-drive stirrer. Then, the reaction mixture was cooled to room temperature, diluted with CH_2Cl_2 (15 mL), the solvent (13 mL) was decanted from the precipitate, repeating this procedure five times. The combined organic phases were washed with 1% aqueous HCl (10 mL) and water (2×15 mL) and dried with Na_2SO_4. The solvent was evaporated *in vacuo* of a water-jet pump. The residue was subjected to chromatography using gradient 5→30% ethyl acetate in light petroleum. The yields of the products are given in Table 1.

Peroxides **2f—i** were obtained similarly using 0.594—1.148 g (0.4 mol of [Cu] per 1 mol of the substrate) of the catalyst. The yields of the products are given in Table 1.

Synthesis of peroxides using a regenerated catalyst. The catalyst $Cu(ClO_4)_2 \cdot 6H_2O/SiO_2$ (687 mg, 0.2 mol of $Cu(ClO_4)_2$ per 1 mol of diketone **1d**) was added to a solution of diketone **1d** (500 mg, 2.63 mmol) in the $CHCl_3$—MeCN solvent system (7 mL, 10 : 1 v/v) (in the 2—6 cycles, a catalyst regenerated from the preceding cycle was used), the mixture was brought to reflux and 70% aqueous Bu^{t}OOH (2.04 g, 15.8 mmol, 6 mol of Bu^{t}OOH per 1 mol of **1d**) was added in six portions (0.34 g each) every 1 h. After addition of the last portion, the mixture was refluxed for 1 h. The mixture was subjected to vigorous mechanical stirring using an upper-drive stirrer. Then, the reaction mixture was cooled to room temperature, diluted with CH_2Cl_2 (15 mL), the solvent (13 mL) was decanted from the precipitate, repeating this procedure five times. The combined organic phases were washed with 1% aqueous HCl (10 mL) and water (2×15 mL) and dried with Na_2SO_4. The solvent was evaporated *in vacuo* of a water-jet pump. The residue was subjected to chromatography using gradient 5→30% ethyl acetate in light petroleum. The catalyst was regenerated by evaporation of the residual solvents at room temperature *in vacuo* of a water-jet pump for 30 min. The yields of product **2d** are given in Table 2.

3-(*tert*-Butylperoxy)-3-hexylpentane-2,4-dione (2a). R_f 0.60 (light petroleum—ethyl acetate, 20 : 1). An oil. ^{1}H NMR, δ: 0.83 (t, 3 H, $C\underline{H}_3CH_2$, J = 6.9 Hz); 1.22—1.26 (m, 17 H, 3 CH_3C, $(CH_2)_4$); 1.96—2.03 (m, 2 H, CCH_2); 2.18 (s, 6 H, CH_3CO). ^{13}C NMR, δ: 13.9 ($\underline{C}H_3CH_2$), 22.5, 22.8, 26.5 ($\underline{C}H_3C$), 26.9, 29.4, 31.2, 31.4, 80.7 ($CH_3\underline{C}$), 97.3 ($CH_2\underline{C}$), 203.5 (CO).

3-Allyl-3-(*tert*-butylperoxy)pentane-2,4-dione (2b). R_f 0.65 (light petroleum—ethyl acetate, 20 : 1). An oil. ^{1}H NMR, δ: 1.29 (s, 9 H, CH_3C); 2.16 (s, 6 H, CH_3CO); 2.79 (d, 2 H, CH_2C, J = 7.3 Hz); 5.04—5.10 (m, 2 H, $C\underline{H}_2CH$); 5.65—5.79 (m, 1 H, CH). ^{13}C NMR, δ: 26.5 ($\underline{C}H_3C$), 26.9 ($\underline{C}H_3CO$), 35.6 ($\underline{C}H_2C$), 80.9 ($CH_3\underline{C}$), 97.0 ($CH_2\underline{C}$), 119.1 ($\underline{C}H_2CH$), 131.5 (CH), 202.7 (CO).

Ethyl 4-acetyl-4-(*tert*-butylperoxy)-5-oxohexanoate (2c). R_f 0.68 (light petroleum—ethyl acetate, 10 : 1). An oil. ^{1}H NMR, δ: 1.20 (t, 3 H, $C\underline{H}_3CH_2$, J = 7.3 Hz); 1.27 (s, 9 H, CH_3C); 2.18 (s, 6 H, CH_3CO); 2.24—2.38 (m, 4 H, $C\underline{H}_2C\underline{H}_2$); 4.07 (q, 2 H, CH_2O, J = 7.3 Hz). ^{13}C NMR, δ: 14.1 ($\underline{C}H_3CH_2$), 26.3 ($\underline{C}H_2C$), 26.4 ($\underline{C}H_3C$), 26.7 ($\underline{C}H_3CO$), 28.2 ($\underline{C}H_2C$), 60.5 (CH_2O), 81.0 ($CH_3\underline{C}$), 96.2 (C), 172.6 (COO), 202.6 ($\underline{C}OCH_3$).

3-Benzyl-3-(*tert*-butylperoxy)pentane-2,4-dione (2d). R_f 0.56 (light petroleum—ethyl acetate, 20 : 1). An oil. ^{1}H NMR, δ: 1.33 (s, 9 H, CH_3C); 1.97 (s, 6 H, CH_3CO); 3.35 (s, 2 H, CH_2); 7.15—7.23 (m, 5 H, CH_{Ar}). ^{13}C NMR, δ: 26.6 ($\underline{C}H_3C$), 27.2 ($\underline{C}H_3CO$), 37.0 (CH_2), 81.3 ($CH_3\underline{C}$), 97.0 ($CH_2\underline{C}$), 126.7, 128.0, 130.5, 135.0 (C_{Ar}), 203.3 (CO).

3-(*tert*-Butylperoxy)-3-(4-methylbenzyl)pentane-2,4-dione (2e). R_f 0.47 (light petroleum—ethyl acetate, 20 : 1). An oil. ^{1}H NMR, δ: 1.33 (s, 9 H, CH_3C); 1.98 (s, 6 H, CH_3CO); 2.29 (s, 3 H); 3.31 (s, 2 H, CH_2); 7.05 (m, 4 H, CH_{Ar}). ^{13}C NMR, δ: 21.0, 26.7 ($\underline{C}H_3C$), 27.3 ($\underline{C}H_3CO$), 36.7 (CH_2), 81.3 ($CH_3\underline{C}$), 97.0 ($CH_2\underline{C}$), 128.8, 130.4, 131.8, 136.3 (C_{Ar}), 203.6 (CO).

Ethyl 2-(*tert*-butylperoxy)-2-methyl-3-oxobutanoate (2f). R_f 0.77 (light petroleum—ethyl acetate, 10 : 1). An oil. ^{1}H NMR, δ: 1.20—1.25 (m, 12 H, 3 CH_3C, $C\underline{H}_3CH_2$); 1.54 (s, 3 H, CH_3); 2.24 (s, 3 H, CH_3); 4.17 (q, 2 H, $CH_3C\underline{H}_2$, J = 7.3 Hz). ^{13}C NMR, δ: 13.9 (CH_3), 18.2 (CH_3), 25.5 (CH_3), 26.3 ($\underline{C}H_3C$), 61.6 (OCH_2), 80.6 ($CH_3\underline{C}$), 89.6 (C), 167.9 (COO), 203.6 (CO).

Ethyl 2-acetyl-2-(*tert*-butylperoxy)hexanoate (2g). R_f 0.79 (light petroleum—ethyl acetate, 20 : 1). An oil. ^{1}H NMR, δ: 0.86 (t, 3 H, $C\underline{H}_3CH_2CH_2$, J = 7.3 Hz); 1.18—1.33 (m, 16 H, CH_3C, $C\underline{H}_3CH_2O$, $CH_3C\underline{H}_2C\underline{H}_2$); 1.99—2.14 (m, 2 H, CH_2C); 2.22 (s, 3 H, CH_3CO); 4.17 (q, 2 H, CH_2O, J = 7.3 Hz). ^{13}C NMR, δ: 13.8, 14.0 (CH_3), 22.2 ($CH_3\underline{C}H_2CH_2$), 24.9 ($\underline{C}H_3CO$), 26.4 ($\underline{C}H_3C$), 30.8 ($\underline{C}H_2C$), 61.4 (CH_2O), 80.5 ($CH_3\underline{C}$), 92.1 (C), 167.6 (COO), 203.5 (CO).

Ethyl 2-(*tert*-butylperoxy)-2-(2-cyanoethyl)-3-oxobutanoate (2h). R_f 0.48 (light petroleum—ethyl acetate, 10 : 1). An oil. ^{1}H NMR, δ: 1.20—1.24 (m, 12 H, CH_3C, $C\underline{H}_3CH_2O$); 2.24 (s, 3 H, CH_3CO); 2.30—2.35 (m, 2 H, CH_2CH_2); 2.48 (t, 2 H, CH_2CH_2, J = 7.33 Hz); 4.18 (q, 2 H, CH_2O, J = 7.3 Hz). ^{13}C NMR, δ: 11.3 ($NC\underline{C}H_2$), 13.7 ($\underline{C}H_3CH_2$), 25.9, 26.2, 26.5 ($\underline{C}H_2C$, $\underline{C}H_3C$, $\underline{C}H_3CO$), 62.2 (CH_2O), 81.3 ($CH_3\underline{C}$), 90.4 ($CH_2\underline{C}$), 118.9 (CN), 165.8 (COO), 201.0 (CO).

Ethyl 2-benzyl-2-(*tert*-butylperoxy)-3-oxobutanoate (2i). R_f 0.60 (light petroleum—ethyl acetate, 10 : 1). An oil. ^{1}H NMR, δ: 1.22 (t, 3 H, $C\underline{H}_3CH_2$, J = 7.3 Hz); 1.30 (s, 9 H, CH_3C); 1.89 (s, 3 H, CH_3CO); 3.33 (d, 1 H, CH_2C, J = 13.9 Hz); 3.56 (d, 1 H,

CH_2C, J = 13.9 Hz); 4.11—4.24 (m, 2 H, CH_2O); 7.16—7.26 (m, 5 H, CH_{Ar}). ^{13}C NMR, δ: 13.9 ($\underline{C}H_3CH_2$), 26.6 ($\underline{C}H_3C$), 27.1 ($\underline{C}H_3CO$), 37.1 ($C_{Ar}\underline{C}H_2$), 61.6 ($CH_3\underline{C}H_2$), 81.1 ($CH_3\underline{C}$), 92.6 ($CH_2\underline{C}$), 126.7, 127.9, 130.6, 134.9 (C_{Ar}), 167.6 (COO), 203.5 (CO).

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