

SUPPORTING INFORMATION (Part 1/2)

AUTHOR NAMES Alexander O. Terent'ev,^a Dmitry A. Borisov,^a Ivan A. Yaremenko,^a Vladimir V. Chernyshev,^{b,c} Gennady I. Nikishin^a.*

AUTHOR ADDRESSES

^a N.D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 47 Leninsky prosp.,
119991 Moscow, Russian Federation

^b Department of Chemistry, Moscow State University, 119992 Moscow, Russian Federation

^c A.N. Frumkin Institute of Physical Chemistry and Electrochemistry, 31 Leninsky prosp., 119991
Moscow, Russian Federation

Table of contents

General methods	S3
Synthesis of β-dicarbonyl compounds 1-3	S4
NMR spectra of β-dicarbonyl compounds 1-3	S6
Synthesis of ethyl 2-benzyl-2-(<i>tert</i>-butylperoxy)-3-oxobutanoate, 4a (Table 1, entries 1-26)	S9
Synthesis of 3-benzyl-3-(<i>tert</i>-butylperoxy)pentane-2,4-dione, 5a (Table 2, entries 1-15)	S9
Synthesis diethyl 2-benzyl-2-(<i>tert</i>-butylperoxy)malonate, 6a (Table 3, entries 1-7)	S10
General procedure for the synthesis of ethyl 2-substituted-2-(<i>tert</i>-butylperoxy)-3-oxobutanoates, 4 (Table 4)	S10
General procedure for the synthesis of 3-substituted-3-(<i>tert</i>-butylperoxy)pentane-2,4-diones, 5 (Table 4)	S10
General procedure for the synthesis of diethyl 2-substituted-2-(<i>tert</i>-butylperoxy)malonates, 6 (Table 4)	S11
Synthesis of 5a from bis-(3-benzyl-2,4-pentanediono)-copper(II)	S11
Synthesis of 5a from 2a with the use of bis-(3-benzyl-2,4-pentanediono)-copper(II) as catalyst	S12
Synthesis of ethyl 2-benzyl-2-(<i>tert</i>-butylperoxy)-3-oxobutanoate by peroxidation of α-benzylacetooacetic ester 1a in the presence of a fivefold molar excess of allyl acetate.	S12
Analytical data of peroxides 4-6	S13
X-Ray analysis of 3-(<i>tert</i>-butylperoxy)-3-(4-nitrobenzyl)pentane-2,4-dione, 5b	S18

General methods

NMR spectra were recorded on commercial instruments (300.13 MHz for ¹H, 75.48 MHz for ¹³C) in CDCl₃. The TLC analysis was carried out on standard silica gel chromatography plates. The melting points were determined on a Kofler hot-stage apparatus.

High resolution mass spectra (HR MS) were measured using electrospray ionization (ESI) [Belyakov, P.A.; Kadentsev, V.I.; Chizhov, A.O.; Kolotyrkina, N.G.; Shashkov, A.S.; Ananikov, V.P. *Mendeleev Commun.* **2010**, *20*, 125 - 131]. The measurements were done in a positive ion mode (interface capillary voltage – 4500 V); mass range from m/z 50 to m/z 3000 Da; external calibration was done with Electrospray Calibrant Solution. A syringe injection was used for solutions in acetonitrile (flow rate 3 µL/min). Nitrogen was applied as a dry gas; interface temperature was set at 180 °C.

Chromatography was performed on silica gel (63-200 mesh). Acetylacetone, acetoacetic ester, diethyl malonate, Cu(OAc)₂×H₂O, Cu(ClO₄)₂×6H₂O, Cu(BF₄)₂×6H₂O, Cu(acac)₂, CuCl, CuCl₂×2H₂O, CuSO₄×5H₂O, Mn(OAc)₂×4H₂O, FeCl₃, Fe(acac)₃, Co(OAc)₂, Co(ClO₄)₂×6H₂O, Co(acac)₂, CoCl₂×6H₂O, H₇[P(Mo₂O₇)₆]×nH₂O, RuCl₃×nH₂O, MgClO₄, KClO₄, CH₂Cl₂, petroleum ether (PE), hexane, ethyl acetate (EA), EtOH, CH₃CN, CH₃COOH, 70 % aqueous Bu^tOOH solution, benzyl- and alkylbromides, acrylonitrile, and ethyl acrylate were purchased from commercial supplier.

To prepare dry Bu^tOOH a 70% aqueous Bu^tOOH solution was extracted twice with the equal volume of CH₂Cl₂, dried over MgSO₄, and filtered. The filtrate was evaporated using a water-jet vacuum pump at 0-10°C for 1h.

Synthesis of β -dicarbonyl compounds 1-3

β -Dicarbonyl compounds **1-3** were prepared in accordance with known methods.

1a, Martin, V. A.; Murray, D. H.; Pratt, N. E.; Zhao, Y.-B.; Albizati, K. F. *J. Am. Chem. Soc.* **1990**, *112*, 6965–6978.

1b, Clark, C. M.; Dobney, J.; Johnson, A. *J. Chem. Soc.* **1962**, 126–130.

1c, Renfrow, W. B.; Renfrow, A. *J. Am. Chem. Soc.* **1946**, *68*, 1801–1804.

1d, Bachmann, W. E.; Dreiding, A. S. *J. Org. Chem.* **1948**, *13*, 317–328.

1e, Nelson, J. H.; Howells, P. N.; DeLullo, G. C.; Landen, G. L.; Henry, R. A. *J. Org. Chem.* **1980**, *45*, 1246–1249.

1f, Albertson, N. F. *J. Am. Chem. Soc.* **1950**, *72*, 2594–2599.

2a, House, H.O.; Gannon, W.F. *J. Org. Chem.* **1958**, *23*, 879 – 884.

2b, Marquet, J.; Moreno-Manas, M.; Pacheco, P.; Prat, M.; Katritzky, A.R.; Brycki, B. *Tetrahedron* **1990**, *46*, 5333 – 5346.

2d, Kaiho, T.; Sannohe, K.; Kajiya, S.; Suzuki, T.; Otsuka, K.; Ito, T., Kamiya, J., Maruyama, M. *J. Med. Chem.* **1989**, *32*, 351 – 357.

2e, Nelson, J. H.; Howells, P. N.; DeLullo, G. C.; Landen, G. L.; Henry, R. A. *J. Org. Chem.* **1980**, *45*, 1246–1249.

2g, Kluiber, R.W.; Oberender, F., Rossi, C. *J. Org. Chem.* **1960**, *25*, 1069–1070.

2h, Kalaitzakis, D.; Rozzell, J. D.; Smonou, I.; Kambourakis, S. *Adv. Synth. Cat.* **2006**, *348*, 1958–1969.

3a, Wu, Z.; Minhas, G. S.; Wen, D.; Jiang, H.; Chen, K.; Zimniak, P.; Zheng, J. *J. Med. Chem.* **2004**, *47*, 3282–3294.

3e, Nelson, J. H.; Howells, P. N.; DeLullo, G. C.; Landen, G. L.; Henry, R. A. *J. Org. Chem.* **1980**, *45*, 1246–1249.

3f, Michael, J. P.; Koning, C. B.; van der Westhuyzen, C. W.; Fernandes, M. A. *J. Chem. Soc., Perkin Trans. 1*, **2001**, 2055–2062.

3h, Linstead, R. P.; Rydon, H. N. *J. Chem. Soc.* **1933**, 580–586.

NMR spectra of β -dicarbonyl compounds 1-3

Ethyl 2-benzyl-3-oxobutanoate, 1a

Colorless oil.

^1H NMR (300.13 MHz, CDCl_3), δ : 1.18 (t, 3H, $J = 7.3$ Hz), 2.16 (s, 3H), 3.15 (d, 2H, $J = 8.1$ Hz), 3.77 (t, 1H, $J = 7.3$ Hz), 4.12 (q, 2H, $J = 7.1$ Hz), 7.11-7.30 (m, 5H).

Ethyl 2-(4-nitrobenzyl)-3-oxobutanoate, 1b

Yellowish crystals. $\text{Mp} = 41\text{-}42$ $^{\circ}\text{C}$.

^1H NMR (300.13 MHz, CDCl_3), δ : 1.19 (t, 3H, $J = 7.3$ Hz), 2.21 (s, 3H), 3.15-3.30 (m, 2H), 3.77 (t, 1H, $J = 7.3$ Hz), 4.08-4.20 (m, 2H), 7.34 (d, 2H, $J = 8.8$ Hz), 8.11 (d, 2H, $J = 8.8$ Hz).

Ethyl 2-acetylhexanoate, 1c

Colorless oil.

^1H NMR (300.13 MHz, CDCl_3), δ : 0.85 (t, 3H, $J = 6.6$ Hz), 1.16-1.36 (m, 7H), 1.73-1.87 (m, 2H), 2.17 (s, 3H), 3.34 (t, 1H, $J = 7.3$ Hz), 4.14 (q, 2H, $J = 7.3$ Hz).

Methyl 2-oxocyclohexanecarboxylate, 1d

Colorless oil.

^1H NMR (300.13 MHz, CDCl_3), δ : 1.51-1.70 (m, 4H), 2.14-2.28 (m, 4H), 3.71 (s, 3H), 12.12 (s, 1H).

Ethyl 2-acetyl-5-oxohexanoate, 1e

Colorless oil.

^1H NMR (300.13 MHz, CDCl_3), δ : 1.19 (t, 3H, $J = 7.0$ Hz), 1.94-2.03 (m, 2H), 2.05 (s, 3H), 2.16 (s, 3H), 2.42 (t, 2H, $J = 7.0$ Hz), 3.41 (t, 1H, $J = 7.0$ Hz), 4.12 (q, 2H, $J = 7.3$ Hz).

Ethyl 2-(2-cyanoethyl)-3-oxobutanoate, 1f

Colorless oil.

^1H NMR (300.13 MHz, CDCl_3), δ : 1.22 (t, 3H, $J = 7.0$ Hz), 1.97-2.14 (m, 2H), 2.22 (s, 3H), 2.38 (t, 2H, $J = 7.0$ Hz), 3.58 (t, 1H, $J = 7.0$ Hz), 4.16 (q, 2H, $J = 7.1$ Hz).

3-Benzylpentane-2,4-dione, 2a

Colorless oil.

¹H NMR (300.13 MHz, CDCl₃), δ: 2.08 (s, 3H), 2.13 (s, 3H), 3.15 (d, 1H, *J* = 7.3 Hz), 3.67 (s, 1H), 4.03 (t, 0.5H, *J* = 7.3 Hz), 7.10-7.42 (m, 5H), 16.85-16.87 (br. s, 0.5H).

3-(4-Nitrobenzyl)pentane-2,4-dione, 2b

Slightly yellow crystals. Mp= 90-91 °C.

¹H NMR (300.13 MHz, CDCl₃), δ: 2.05 (s, 6H), 3.76 (s, 2H), 7.31 (d, 2H, *J* = 8.1 Hz), 8.17 (d, 2H, *J* = 8.8 Hz), 16.84-16.86 (br. s, 1H).

2-Acetylhexanone, 2d

Colorless oil.

¹H NMR (300.13 MHz, CDCl₃), δ: 1.57-1.69 (m, 4H), 2.07 (s, 3H), 2.22-2.32 (m, 4H), 15.85-15.87 (br.s, 1H).

3-Acetylheptane-2,6-dione, 2e

Colorless oil.

¹H NMR (300.13 MHz, CDCl₃), δ: 1.98-2.16 (m, 11H), 2.40 (t, 2H, *J* = 7.0 Hz), 3.63 (t, 0.8H, *J* = 7.0 Hz), 16.64 (br. s, 0.2H).

Ethyl 4-acetyl-5-oxohexanoate, 2g

Colorless oil.

¹H NMR (300.13 MHz, CDCl₃), δ: 1.16 -1.24 (m, 3H), 2.03-2.57 (m, 10H), 3.69 (t, 0.7H, *J* = 7.0 Hz), 4.02-4.13 (m, 2H), 16.69-16.71 (br. s, 0.3H).

3-Allylpentane-2,4-dione, 2h

Colorless oil.

¹H NMR (300.13 MHz, CDCl₃), δ: 2.04 (s, 3H), 2.13 (s, 3H), 2.53 (m, 1H), 2.93 (d, 1H, *J* = 5.1 Hz), 3.68 (t, 0.5H, *J* = 7.3 Hz), 4.86-5.98 (m, 3H), 16.67-16.69 (br. s, 0.5H).

Diethyl 2-benzylmalonate, 3a

Colorless oil.

¹H NMR (300.13 MHz, CDCl₃), δ: 1.18 (t, 6H, *J* = 7.3 Hz), 3.21 (d, 2H, *J* = 8.1 Hz), 3.64 (t, 1H, *J* = 7.7 Hz), 4.13 (q, 4H, *J* = 7.1 Hz), 7.14-7.29 (m, 5H).

Diethyl 2-(3-oxobutyl)malonate, 3e

Colorless oil.

¹H NMR (300.13 MHz, CDCl₃), δ: 1.16 (t, 6H, *J* = 7.3 Hz), 1.99-2.13 (m, 5H), 2.45 (t, 2H, *J* = 7.3 Hz), 3.28 (t, 1H, *J* = 7.3 Hz), 4.09 (q, 4H, *J* = 7.3 Hz).

Diethyl 2-(2-cyanoethyl)malonate, 3f

Colorless oil.

¹H NMR (300.13 MHz, CDCl₃), δ: 1.24 (t, 6H, *J* = 7.0 Hz), 2.20 (q, 2H, *J* = 7.3 Hz), 2.46 (t, 2H, *J* = 7.3 Hz), 3.45 (t, 1H, *J* = 7.3 Hz), 4.18 (q, 4H, *J* = 6.8 Hz).

Diethyl 2-allylmalonate, 3h

Colorless oil.

¹H NMR (300.13 MHz, CDCl₃), δ: 1.21 (t, 6H, *J* = 7.0 Hz), 2.59 (t, 2H, *J* = 7.0 Hz), 3.36 (t, 1H, *J* = 7.7 Hz), 4.14 (q, 4H, *J* = 7.1 Hz), 4.96-5.11 (m, 2H), 5.65-5.80 (m, 1H).

Bis-(3-benzyl-2,4-pentanediono)-copper(II), dark crystals, Mp= 200-201 °C.

Mp [Dryden, R.; Winston, A. *J. Org. Chem.* **1958**, 62, 635–637] = 203.0-203.5 °C.

Synthesis of ethyl 2-benzyl-2-(*tert*-butylperoxy)-3-oxobutanoate, **4a (Table 1, entries 1-26).**

A 70 % aqueous Bu^tOOH solution (0.35-0.88 g, 2-5 mol per mole of **1a**) was added to a solution of 2-benzyl-3-oxobutanoate **1a** (0.3 g, 1.36 mmol) and catalyst (Cu(OAc)₂×H₂O, Cu(ClO₄)₂×6H₂O, Cu(BF₄)₂×6H₂O, Cu(acac)₂, CuCl, CuCl₂×2H₂O, CuSO₄×5H₂O, Mn(OAc)₂×4H₂O, FeCl₃, Fe(acac)₃ (0.05-0.2 mol per mole of **1a**) in the solvent (5 mL; CH₃CN, EtOH, CH₃COOH). The reaction mixture was refluxed at 79-119 °C for 0.5-2 h, cooled to 20-25 °C, poured into water (40 mL), stirred, and extracted with CH₂Cl₂ (3×10 mL). The combined extracts were washed with water (3×10 mL), dried over Na₂SO₄, and filtered. The filtrate was evaporated using a water-jet vacuum pump. The residue was chromatographed using a petroleum ether-ethyl acetate system with an increase in the fraction of the latter solvent from 0 to 20 %.

Synthesis of 3-benzyl-3-(*tert*-butylperoxy)pentane-2,4-dione, **5a (Table 2, entries 1-15).**

A 70 % aqueous Bu^tOOH solution (0.41-1.03 g, 2-5 mol per mole of **2a**) was added to a solution of 3-benzylpentane-2,4-dione **2a** (0.3 g, 1.58 mmol) and catalyst (Cu(OAc)₂×H₂O, Cu(ClO₄)₂×6H₂O, Cu(BF₄)₂×6H₂O, Cu(acac)₂, CoCl₂×6H₂O, Co(acac)₂, Co(ClO₄)₂×6H₂O, Fe(acac)₃, FeCl₃, Mn(OAc)₂×4H₂O; 0.02-0.5 mol per mole of **2a**) in CH₃CN (5 mL). The reaction mixture was refluxed at 79-81 °C for 0.25-2 h, cooled to 20-25 °C, poured into water (40 mL), stirred, and extracted with CH₂Cl₂ (3×10 mL). The combined extracts were washed with water (3×10 mL), dried over Na₂SO₄, and filtered. The filtrate was evaporated using a water-jet vacuum pump. The residue was chromatographed using a petroleum ether-ethyl acetate system with an increase in the fraction of the latter solvent from 0 to 20 %.

Synthesis diethyl 2-benzyl-2-(*tert*-butylperoxy)malonate, **6a (Table 3, entries 1-7).**

A 70 % aqueous Bu^tOOH solution (0.31-0.78 g, 2-5 mol per mole of **3a**) was added to a solution of diethyl 2-benzylmalonate **3a** (0.3 g, 1.2 mmol) and Cu(ClO₄)₂×6H₂O (45-225 mg, 0.1-0.5 mol per mole of **3a**) in CH₃CN (5 mL). The reaction mixture was refluxed at 79-81 °C for 1-2 h, cooled to 20-25 °C, poured into water (40 mL), stirred, and extracted with CH₂Cl₂ (3×10 mL). The combined extracts were washed with water (3×10 mL), dried over Na₂SO₄, and filtered. The filtrate was evaporated using a water-jet vacuum pump. The residue was chromatographed using a petroleum ether-ethyl acetate system with an increase in the fraction of the latter solvent from 0 to 20 %.

General procedure for the synthesis of ethyl 2-substituted-2-(*tert*-butylperoxy)-3-oxobutanoates, **4 (Table 4).**

A 70 % aqueous Bu^tOOH solution (2 mol per mole of **1**) was added to a solution of ethyl 2-substituted-3-oxobutanoates **1** (0.3 g) and Cu(ClO₄)₂×6H₂O (0.1 mole per mole of **1**) in CH₃CN (5 mL). The reaction mixture was refluxed at 79-81 °C for 1 h, cooled to 20-25 °C, poured into water (40 mL), stirred, and extracted with CH₂Cl₂ (3×10 mL). The combined extracts were washed with water (3×10 mL), dried over Na₂SO₄, and filtered. The filtrate was evaporated using a water-jet vacuum pump. The residue was chromatographed using a petroleum ether-ethyl acetate system with an increase in the fraction of the latter solvent from 0 to 20 %.

General procedure for the synthesis of 3-substituted-3-(*tert*-butylperoxy)pentane-2,4-diones, **5 (Table 4).**

A 70 % aqueous Bu^tOOH solution (3 mol per mole of **2**) was added to a solution of 3-substituted-2,4-dione **2** (0.3 g) and catalyst Cu(ClO₄)₂×6H₂O (0.05 mol per mole of **2**) in CH₃CN (5 mL). The reaction mixture was refluxed at 79-81 °C for 15 min, cooled to 20-25 °C, poured into water (40 mL), stirred, and

extracted with CH_2Cl_2 (3×10 mL). The combined extracts were washed with water (3×10 mL), dried over Na_2SO_4 , and filtered. The filtrate was evaporated using a water-jet vacuum pump. The residue was chromatographed using a petroleum ether-ethyl acetate system with an increase in the fraction of the latter solvent from 0 to 20 %.

General procedure for the synthesis of diethyl 2-substituted-2-(*tert*-butylperoxy)malonates, **6 (Table 4).**

A 70 % aqueous Bu^tOOH solution (5 mol per mole of **3**) was added to a solution of diethyl 2-substituted malonate **3** (0.3 g) and catalyst $\text{Cu}(\text{ClO}_4)_2\text{x}6\text{H}_2\text{O}$ (0.4 mol per mole of **3**) in CH_3CN (5 mL). The reaction mixture was refluxed at 79-81 °C for 1 h, cooled to 20-25 °C, poured into water (40 mL), stirred, and extracted with CH_2Cl_2 (3×10 mL). The combined extracts were washed with water (3×10 mL), dried over Na_2SO_4 , and filtered. The filtrate was evaporated using a water-jet vacuum pump. The residue was chromatographed using a petroleum ether-ethyl acetate system with an increase in the fraction of the latter solvent from 0 to 20 %.

Synthesis of **5a from bis-(3-benzyl-2,4-pentanediono)-copper(II).**

A 70 % aqueous Bu^tOOH solution (0.52 g, 4.08 mmol, 6 mol per mole of copper complex) was added to a suspension of bis-(3-benzyl-2,4-pentanediono)-copper(II) (0.3 g, 0.68 mmol) in CH_3CN (5 mL). The reaction mixture was refluxed at 79-81 °C for 15 min, cooled to 20-25 °C, poured into water (40 mL), stirred, and extracted with CH_2Cl_2 (3×10 mL). The combined extracts were washed with water (3×10 mL), dried over Na_2SO_4 , and filtered. The filtrate was evaporated using a water-jet vacuum pump. The residue was chromatographed using a petroleum ether-ethyl acetate system with an increase in the fraction of the latter solvent from 0 to 20 %. Product **5a** was obtained in 44 % yield (0.17 g, 0.61 mmol).

Synthesis of **5a from **2a** with the use of bis-(3-benzyl-2,4-pentanediono)-copper(II) as catalyst.**

A 70 % aqueous Bu^tOOH solution (0.61 g, 4.74 mmol, 3 mol per mole of **2a**) was added to a solution of bis-(3-benzyl-2,4-pentanediono)-copper(II) (0.035 g, 0.08 mmol, 0.05 mol per mole of **2a**) and **2a** (0.3 g, 1.58 mmol) in CH₃CN (5 mL). The reaction mixture was refluxed at 79-81 °C for 1 h, cooled to 20-25 °C, poured into water (40 mL), stirred, and extracted with CH₂Cl₂ (3×10 mL). The combined extracts were washed with water (3×10 mL), dried over Na₂SO₄, and filtered. The filtrate was evaporated using a water-jet vacuum pump. The residue was chromatographed using a petroleum ether-ethyl acetate system with an increase in the fraction of the latter solvent from 0 to 20 %. Product **5a** was obtained in 23 % yield (0.1 g, 0.36 mmol).

Synthesis of ethyl 2-benzyl-2-(*tert*-butylperoxy)-3-oxobutanoate by peroxidation of α -benzylacetooacetic ester **1a in the presence of a fivefold molar excess of allyl acetate.**

A 70 % aqueous Bu^tOOH solution (0.35 g, 2.72 mmol, 2 mol per mole of **1a**) was added to a solution of 2-benzyl-3-oxobutanoate **1a** (0.3 g, 1.36 mmol), allyl acetate (0.68 g, 6.8 mmol), and Cu(ClO₄)₂×6H₂O (0.05 g, 0.136 mmol, 0.1 mol per mole of **1a**) in CH₃CN (5 mL). The reaction mixture was refluxed at 79-81 °C for 1 h, cooled to 20-25 °C, poured into water (40 mL), stirred, and extracted with CH₂Cl₂ (3×10 mL). The combined extracts were washed with water (3×10 mL), dried over Na₂SO₄, and filtered. The filtrate was evaporated using a water-jet vacuum pump. The residue was chromatographed using a petroleum ether-ethyl acetate system with an increase in the fraction of the latter solvent from 0 to 20 %. Product **4a** was obtained in 86 % yield (0.36 g, 1.18 mmol).

Analytical data of Peroxides 4-6

Ethyl 2-benzyl-2-(*tert*-butylperoxy)-3-oxobutanoate, 4a

Oil. R_f = 0.68 (TLC, hexane – EA, 5:1).

¹H NMR (300.13 MHz, CDCl₃), δ: 1.21 (t, 3H, *J* = 7.3 Hz), 1.30 (s, 9H), 1.89 (s, 3H), 3.44 (dd, 2H, *J* = 13.9, 69.7 Hz), 4.10-4.23 (m, 2H), 7.16-7.26 (m, 5H). ¹³C NMR (75.48 MHz, CDCl₃), δ: 13.8, 26.5, 27.0, 37.1, 61.5, 81.0, 92.6, 126.6, 127.9, 130.6, 134.9, 167.5, 203.4. Anal. Calcd for C₁₇H₂₄O₅: C, 66.21; H, 7.84. Found: C, 66.32; H, 7.89.

Ethyl 2-(*tert*-butylperoxy)-2-(4-nitrobenzyl)-3-oxobutanoate, 4b

Oil. R_f = 0.60 (TLC, hexane – EA, 5:1).

¹H NMR (300.13 MHz, CDCl₃), δ: 1.23 (t, 3H, *J* = 7.0 Hz), 1.30 (s, 9H), 1.97 (s, 3H), 3.56 (dd, 2H, *J* = 13.9, 51.4 Hz), 4.12-4.24 (m, 2H), 7.39 (d, 2H, *J* = 8.1 Hz), 8.10 (d, 2H, *J* = 8.8 Hz). ¹³C NMR (75.48 MHz, CDCl₃), δ: 13.9, 26.5, 26.9, 36.4, 62.0, 81.6, 92.4, 123.0, 131.5, 143.2, 147.0, 166.8, 202.3. Anal. Calcd for C₁₇H₂₃NO₇: C, 57.78; H, 6.56; N, 3.96. Found: C, 57.83; H, 6.43; N, 3.90. HRMS (ESI): m/z [M+Na]⁺: calculated for [C₁₇H₂₃NNaO₇]⁺: 376.1367; found: 376.1367.

Ethyl 2-acetyl-2-(*tert*-butylperoxy)hexanoate, 4c

Oil. R_f = 0.69 (TLC, hexane – EA, 10:1).

¹H NMR (300.13 MHz, CDCl₃), δ: 0.82 (t, 3H, *J* = 7.0 Hz), 1.08-1.34 (m, 16H), 1.94-2.07 (m, 2H), 2.18 (s, 3H), 4.13 (q, 2H, *J* = 7.0 Hz). ¹³C NMR (75.48 MHz, CDCl₃), δ: 13.7, 13.9, 22.6, 24.8, 26.3, 30.8, 61.3, 80.4, 92.0, 167.5, 203.3. Anal. Calcd for C₁₄H₂₆O₅: C, 61.29; H, 9.55. Found: C, 61.12; H, 9.62. HRMS (ESI): m/z [M+Na]⁺: calculated for [C₁₄H₂₆NaO₅]⁺: 297.1672; found: 297.1679.

Methyl 1-(*tert*-butylperoxy)-2-oxocyclohexanecarboxylate, 4d

White crystals. Mp = 35-36 °C. Rf = 0.71 (TLC, hexane – EA, 10:1).

¹H NMR (300.13 MHz, CDCl₃), δ: 1.24 (s, 9H), 1.59-2.04 (m, 4H), 2.17-2.41 (m, 3H), 2.63-2.77 (m, 1H), 3.75 (s, 3H). ¹³C NMR (75.48 MHz, CDCl₃), δ: 20.6, 26.4, 27.5, 34.5, 39.8, 52.0, 80.7, 89.7, 169.4, 203.2. Anal. Calcd for C₁₂H₂₀O₅: C, 59.00; H, 8.25. Found: C, 58.94; H, 8.27.

Ethyl 2-acetyl-2-(*tert*-butylperoxy)-5-oxohexanoate, 4e

Oil. Rf = 0.55 (TLC, hexane – EA, 5:1).

¹H NMR (300.13 MHz, CDCl₃), δ: 1.16-1.24 (m, 12H), 2.07 (s, 3H), 2.19 (s, 3H), 2.28-2.45 (m, 4H), 4.14 (q, 2H, J = 7.1 Hz). ¹³C NMR (75.48 MHz, CDCl₃), δ: 13.8, 25.0, 26.3, 29.6, 37.2, 61.7, 80.8, 90.9, 167.0, 202.3, 207.1. Anal. Calcd for C₁₄H₂₄O₆: C, 58.32; H, 8.39. Found: C, 58.26; H, 8.42.

Ethyl 2-(*tert*-butylperoxy)-2-(2-cyanoethyl)-3-oxobutanoate, 4f

Oil. Rf = 0.54 (TLC, hexane – EA, 10:1).

¹H NMR (300.13 MHz, CDCl₃), δ: 1.20-1.27 (m, 12H), 2.24 (s, 3H), 2.40 (dt, 4H, J = 8.1, 48.4 Hz), 4.18 (q, 2H, J = 7.0 Hz). ¹³C NMR (75.48 MHz, CDCl₃), δ: 11.3, 13.8, 25.9, 26.2, 26.5, 62.2, 81.4, 90.4, 118.9, 165.9, 201.1. Anal. Calcd for C₁₃H₂₁NO₅: C, 57.55; H, 7.80; N, 5.16. Found: C, 57.47; H, 7.81; N, 5.21. HRMS (ESI): m/z [M+Na]⁺: calculated for [C₁₃H₂₁NNaO₅]⁺: 294.1312; found: 294.1307.

3-Benzyl-3-(*tert*-butylperoxy)pentane-2,4-dione, 5a

Yellowish crystals. Mp = 34-36 °C. Rf = 0.74 (TLC, hexane – EA, 10:1).

¹H NMR (300.13 MHz, CDCl₃), δ: 1.33 (s, 9H), 1.98 (s, 6H), 3.36 (s, 2H), 7.14-7.27 (m, 5H). ¹³C NMR (75.48 MHz, CDCl₃), δ: 26.6, 27.2, 37.1, 81.3, 97.0, 126.7, 128.0, 130.5, 135.0, 203.3. Anal. Calcd for C₁₆H₂₂O₄: C, 69.04; H, 7.97. Found: C, 69.10; H, 7.94.

3-(*tert*-Butylperoxy)-3-(4-nitrobenzyl)pentane-2,4-dione, 5b

White crystals. Mp = 109-110 °C (with decomp.). Rf = 0.64 (TLC, hexane – EA, 5:1).

¹H NMR (300.13 MHz, CDCl₃), δ: 1.33 (s, 9H), 2.03 (s, 6H), 3.48 (s, 2H), 7.35 (d, 2H, *J* = 8.8 Hz), 8.11 (d, 2H, *J* = 8.8 Hz). ¹³C NMR (75.48 MHz, CDCl₃), δ: 26.7, 27.1, 36.6, 81.8, 97.2, 123.2, 131.4, 143.4, 147.1, 202.1. Anal. Calcd for C₁₆H₂₁NO₆: C, 59.43; H, 6.55; N, 4.33. Found: C, 59.49 ; H, 6.50; N, 4.42.

2-Acetyl-2-(*tert*-butylperoxy)cyclohexanone, 5d

Oil. Rf = 0.38 (TLC, hexane – EA, 10:1).

¹H NMR (300.13 MHz, CDCl₃), δ: 1.26 (s, 9H), 1.60-2.17 (m, 6H), 2.23 (s, 3H), 2.26-2.35 (m, 1H), 2.59-2.71 (m, 1H). ¹³C NMR (75.48 MHz, CDCl₃), δ: 20.5, 26.5, 26.7, 27.4, 32.8, 40.4, 80.7, 92.9, 204.6, 206.9. Anal. Calcd for C₁₂H₂₀O₄: C, 63.14; H, 8.83. Found: C, 63.02; H, 8.85. HRMS (ESI): m/z [M+Na]⁺: calculated for [C₁₂H₂₀NaO₄]⁺: 251.1254; found: 251.1255.

3-Acetyl-3-(*tert*-butylperoxy)heptane-2,6-dione, 5e

Oil. Rf = 0.40 (TLC, hexane – EA, 5:1).

¹H NMR (300.13 MHz, CDCl₃), δ: 1.26 (s, 9H), 2.08 (s, 3H), 2.18 (s, 6H), 2.25-2.44 (m, 4H). ¹³C NMR (75.48 MHz, CDCl₃), δ: 25.1, 26.4, 26.7, 29.7, 37.4, 81.0, 95.8, 203.0, 207.2. Anal. Calcd for C₁₃H₂₂O₅: C, 60.45; H, 8.58. Found: C, 60.54; H, 8.62.

Ethyl 4-acetyl-4-(*tert*-butylperoxy)-5-oxohexanoate, 5g

Oil. Rf = 0.53 (TLC, hexane – EA, 10:1).

¹H NMR (300.13 MHz, CDCl₃), δ: 1.17 (t, 3H, *J* = 7.0 Hz), 1.24 (s, 9H), 2.16 (s, 6H), 2.18-2.38 (m, 4H), 4.04 (q, 2H, *J* = 7.0 Hz). ¹³C NMR (75.48 MHz, CDCl₃), δ: 14.0, 26.2, 26.3, 26.6, 28.2, 60.4, 81.0, 96.1,

172.6, 202.5. Anal. Calcd for $C_{14}H_{24}O_6$: C, 58.32; H, 8.39. Found: C, 58.24; H, 8.36. HRMS (ESI): m/z $[M+Na]^+$: calculated for $[C_{14}H_{24}NaO_6]^+$: 311.1465; found: 311.1473.

3-Allyl-3-(*tert*-butylperoxy)pentane-2,4-dione, 5h

Oil. Rf = 0.67 (TLC, hexane – EA, 10:1).

1H NMR (300.13 MHz, $CDCl_3$), δ : 1.27 (s, 9H), 2.14 (s, 6H), 2.77 (d, 2H, J = 7.3 Hz), 4.99-5.08 (m, 2H), 5.61-5.77 (m, 1H). ^{13}C NMR (75.48 MHz, $CDCl_3$), δ : 26.4, 26.8, 35.5, 80.9, 97.0, 119.0, 131.5, 202.6. Anal. Calcd for $C_{12}H_{20}O_4$: C, 63.14; H, 8.83. Found: C, 63.10; H, 8.89. HRMS (ESI): m/z $[M+Na]^+$: calculated for $[C_{12}H_{20}NaO_4]^+$: 251.1254; found: 251.1259.

Diethyl 2-benzyl-2-(*tert*-butylperoxy)malonate, 6a

White crystals. Mp = 44-45 °C. Rf = 0.37 (TLC, hexane – EA, 10:1).

1H NMR (300.13 MHz, $CDCl_3$), δ : 1.20 (t, 6H, J = 7.3 Hz), 1.29 (s, 9H), 3.50 (s, 2H), 4.11-4.21 (m, 4H), 7.14-7.28 (m, 5H). ^{13}C NMR (75.48 MHz, $CDCl_3$), δ : 13.9, 26.5, 37.8, 61.6, 81.0, 87.9, 126.8, 127.9, 130.3, 134.9, 166.9. Anal. Calcd for $C_{18}H_{26}O_6$: C, 63.89; H, 7.74. Found: C, 63.76; H, 7.84.

Diethyl 2-(*tert*-butylperoxy)-2-(3-oxobutyl)malonate, 6e

Oil. Rf = 0.54 (TLC, hexane – EA, 5:1).

1H NMR (300.13 MHz, $CDCl_3$), δ : 1.16-1.29 (m, 15H), 2.11 (s, 3H), 2.40-2.54 (m, 4H), 4.19 (q, 4H). ^{13}C NMR (75.48 MHz, $CDCl_3$), δ : 13.9, 25.9, 26.3, 29.8, 37.1, 61.7, 80.7, 86.3, 167.0, 207.0. Anal. Calcd for $C_{15}H_{26}O_7$: C, 56.59; H, 8.23. Found: C, 56.71; H, 8.30.

Diethyl 2-(*tert*-butylperoxy)-2-(2-cyanoethyl)malonate, 6f

Oil. Rf = 0.50 (TLC, hexane – EA, 5:1).

¹H NMR (300.13 MHz, CDCl₃), δ: 1.17-1.30 (m, 15H), 2.34-2.59 (m, 4H), 4.10-4.30 (m, 4H). ¹³C NMR (75.48 MHz, CDCl₃), δ: 11.3, 13.8, 26.2, 27.8, 62.1, 81.3, 85.4, 118.9, 165.9. Anal. Calcd for C₁₄H₂₃NO₆: C, 55.80; H, 7.69; N, 4.65. Found: C, 55.75; H, 7.56; N, 4.69.

Diethyl 2-allyl-2-(*tert*-butylperoxy)malonate, 6h

Oil. R_f = 0.41 (TLC, hexane – EA, 5:1).

¹H NMR (300.13 MHz, CDCl₃), δ: 1.18-1.27 (m, 15H), 2.91 (d, 2H, *J* = 7.3 Hz), 4.20 (q, 4H, *J* = 7.1 Hz), 5.03-5.13 (m, 2H), 5.68-5.84 (m, 1H). ¹³C NMR (75.48 MHz, CDCl₃), δ: 14.0, 26.3, 36.5, 61.5, 80.7, 87.1, 118.9, 131.3, 166.9. Anal. Calcd for C₁₄H₂₄O₆: C, 58.32; H, 8.39. Found: C, 58.25; H, 8.30.

X-Ray analysis of 3-(*tert*-butylperoxy)-3-(4-nitrobenzyl)pentane-2,4-dione, **5b**

The molecular structure of **5b** has been confirmed by X-ray structure determination. Intensity data set was collected at room temperature using an Enraf-Nonius CAD4 diffractometer (Cu K α radiation, $\lambda = 1.54184 \text{ \AA}$) equipped with a graphite monochromator. The crystal structure was solved by direct methods in orthorhombic space group *Pbca*. Crystallographic programs used for structure solution and refinement, respectively, were *SHELXS97* and *SHELXL97*¹. The structure was refined by full-matrix least-squares refinement on F^2 . Hydrogen atoms were placed geometrically and refined using a riding model with U_{iso} constrained at 1.2 and 1.5 (for methyl) times U_{eq} of the carrier C atom. The crystal data, data collection and refinement parameters for **5b** are given in **Table 1**. The molecular structure of **5b** is shown on **Fig. 1**.

All bond lengths and angles in **5b** are normal and comparable with those observed in related structures found in Cambridge Structural Database (CCDC).² In the crystal structure, weak intermolecular C---H...O hydrogen bonds (**Table 2**) link molecules into corrugated layers parallel to *ac* plane (**Fig. 2**).

Table 1. Crystal data for **5b**.

	5b
empirical formula	C ₁₆ H ₂₁ NO ₆
M _r	323.34
crystal size, mm ³	0.50 x 0.27 x 0.20
crystal form, colour	Prism, colourless
crystal system	orthorhombic
space group	<i>Pbca</i>
unit cell dimensions	
a, Å	7.2714(16)
b, Å	18.978(3)
c, Å	25.506(3)
volume, Å ³	3519.8(10)
Z	8
D _x (Mg m ⁻³)	1.220
μ, mm ⁻¹	0.784
no. reflns independent	3324
no. params	214
GOF	1.057
final <i>R</i> indices [<i>I</i> >2σ(<i>I</i>)]	<i>R</i> = 0.0702, <i>wR</i> = 0.2160

Table 2. Hydrogen-bonding geometry (Å, °).

D-H...A	D-H	H...A	D...A	D-H...A
C7-H7B...O5 ⁱ	0.97	2.62	3.467(6)	146 5_675
C18-H18B...O17 ⁱⁱ	0.97	2.61	3.514(6)	158 6_556

Symmetry codes: (i) 1-*x*, 2-*y*, -*z*; (ii) *x*-1/2, *y*, 1/2-*z*.

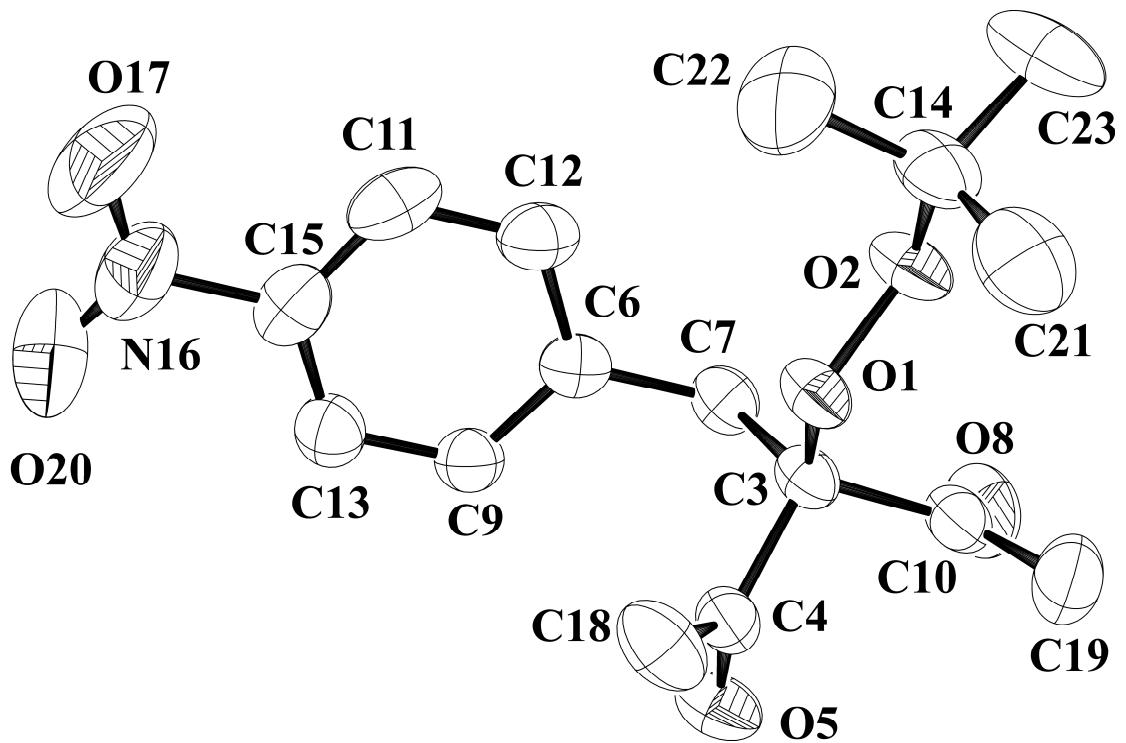
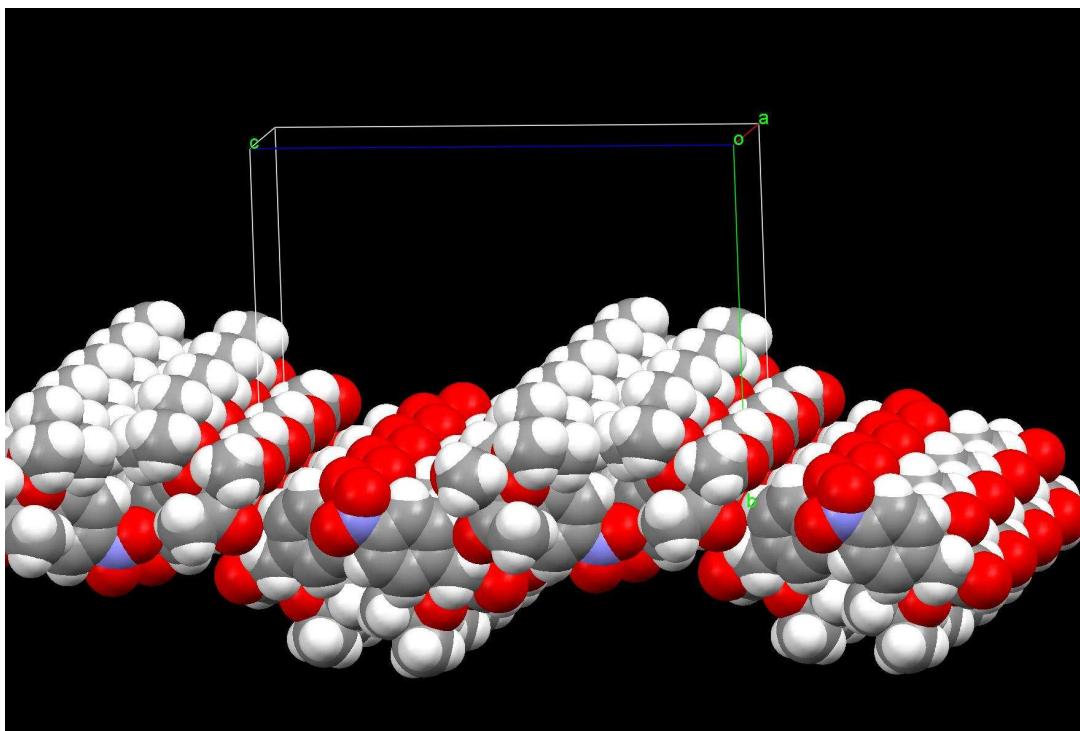
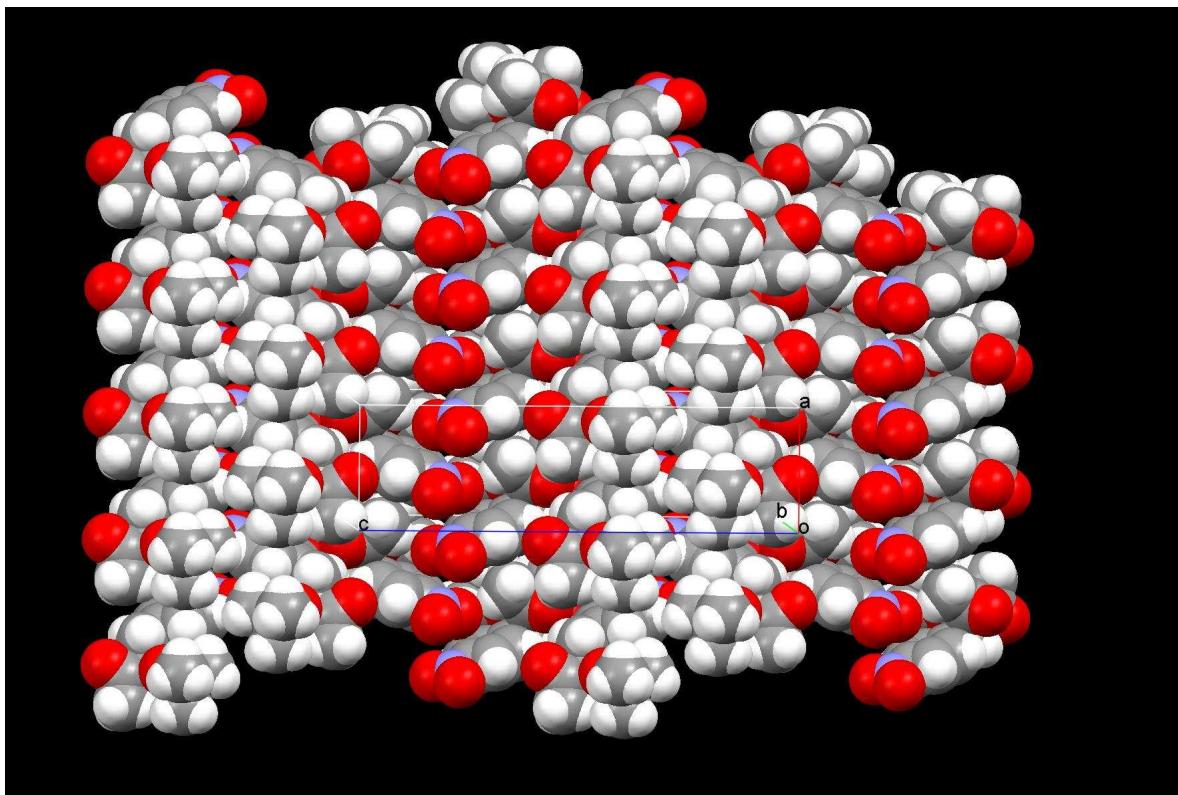


Fig. 1. The molecular structure of **5b**, showing the atomic numbering and 40% probability displacement ellipsoids. H atoms omitted for clarity.



(a)



(b)

Fig. 2. The *Mercury*³ spacefill representation of hydrogen-bonded layer in the crystal structure of **5b** viewed in two orthogonal projections: (a) approximately along axis *a*; (b) approximately along axis *b*.

Crystallographic data for **5b** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 760010. Copies of data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

References.

- (1) Sheldrick, G.M. *Acta Cryst. A*, **2008**, *A64*, 112.
- (2) Allen, F.H. *Acta Cryst. B*, **2002**, *B58*, 380.
- (3) Macrae, C. F., Edgington, P. R., McCabe, P., Pidcock, E., Shields, G. P., Taylor, R., Towler, M. and van de Streek, J. *J. Appl. Cryst.* **2006**, *39*, 453.