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Manganese triacetate as an efficient catalyst for bisperoxidation of styrenes

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A method was developed for the bisperoxidation of styrenes with *tert*-butyl hydroperoxide in the presence of a catalytic amount of manganese(III) acetate. It was shown that compounds of manganese in oxidation states 2, 4, and 7 also catalyze this reaction. Target [1,2-bis(*tert*-butylperoxy)ethyl]arenes were synthesized in yields from 46 to 75%.

Introduction

Due to the ready availability and high efficiency, organic peroxides have been widely used for more than half a century as radical polymerization initiators in the industrial synthesis, for example, of such polymers as polystyrene, polyvinyl chloride, polyacrylates, and high-pressure polyethylene. Organic peroxides are also used for the crosslinking of silicone, acrylonitrile-butadiene, and fluorinated rubbers. A wide variety of commercial monomers and their compositions demands a wide assortment of peroxides, the most well-known of which are organic hydroperoxides, dialkyl peroxides, diacyl peroxides, peroxy esters, peroxydicarbonates, peroxycarbonates, peracetals, cyclic triperoxides, and geminal bishydroperoxides.[1,2]

In the past decades, organic peroxides have got attention from researchers in the fields of medicinal chemistry and pharmacology because these compounds, particularly ozonides and tetraoxanes, were found to exhibit marked antimalarial,[3] anthelmintic,[4] and antitumor activities.[5] Peroxides, particularly derivatives of lower aldehydes and ketones, are still attracting interest also as energy-rich compounds. For instance, the explosive power of triacetone triperoxide is comparable with that of trinitrotoluene.[6]

Due to the tendency of peroxides to decompose, their high sensitivity to reducing agents and variable valence metal ions, and the ease of a large range of transformations accompanied by the O-O bond cleavage, the search for general approaches to the synthesis of peroxides and the selective synthesis of peroxides of the specified structure are difficult problems.

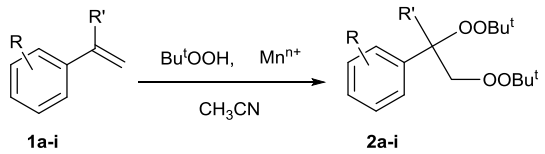
The transition metal (Cu, Mn, Co)/hydroperoxide system was used for the first time by Kharasch in the synthesis of peroxides from alkenes, ketones, and tertiary amines more than six decades ago.[7] Since that time, the research on and application of this peroxidation method were documented in a number of publications. The formation of peroxides was observed in various reactions of hydroperoxides catalyzed by metal salts and their complexes: copper,[8] cobalt,[9] and iron,[10,11] dinuclear nickel complexes,[12] palladium acetate,[13] ruthenium(II)-bipyridine anchored montmorillonite,[14] and metalloporphyrins.[15] Peroxides were synthesized in high yields by the peroxidation of amines, amides, and lactams catalyzed by ruthenium salts.[16] Examples of the synthesis of such compounds are limited by the tendency of peroxides to decompose in the presence of variable valence metals.

In the present study, we developed a new approach to the synthesis of vicinal bis(*tert*-butyl)peroxides from styrenes and *tert*-butyl hydroperoxide using manganese(III) acetate. Manganese(III) acetate is a strong oxidizer. This compound proved to be an efficient reagent in redox and free radical reactions accompanied by the C-C,[17] C-O,[18] and C-N[19] bond formation. The combination of two oxidizing agents, $Mn(OAc)_3$ and TBHP, imparts new properties to the system. These properties were used to oxidize alkenes at the allylic position to form enones.[20]

The known methods for the synthesis of vicinal bisperoxides from styrenes and TBHP are based on the use of palladium acetate,[13] ruthenium(II) bipyridine anchored montmorillonite,[14] dinuclear nickel complexes,[12] and Mn(III) porphyrins.[15] The drawback of the former two approaches, although they provide good yields (65-85% and 30-69%, respectively), is the use of expensive catalysts. In the third approach, the difficult-to-prepare catalyst is employed and, besides, the target bisperoxide is produced in a rather low yield (26%). The reactions with the use of iron(III) or manganese(III) porphyrins (Fe(III)TDCIPP-OAc or Mn(III)TDCIPP-OAc) give the target products with low yields. In the present study, we found that styrenes are selectively peroxidized with high conversion in the reaction with TBHP and manganese(III) acetate to form vicinal bisperoxides ([1,2-bis(*tert*-butylperoxy)ethyl]arenes).

Results and discussion

Vicinal bisperoxides **2a-i** (Scheme 1) were synthesized from styrenes **1a-i** containing substituents of different nature.



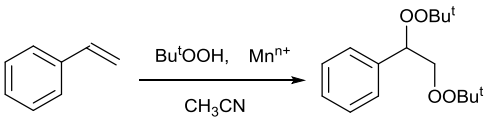
1a-i **2a-i**

a: R = H; R' = H; **b**: R = H; R' = Me; **c**: R = 4-Me; R' = H;
d: R = t-Bu; R' = H; **e**: R = 4-OMe; R' = H; **f**: R = 2-OMe; R' = H;
g: R = H; R' = Ph; **h**: R = 2,3-(CH)$_4$; R' = H; **i**: R = Cl; R' = H

Scheme 1 Synthesis of vicinal bis(*tert*-butyl)peroxides **2a-i** from styrenes **1a-i** and *tert*-butyl hydroperoxide

In order to optimize the reaction conditions, we studied the peroxidation of styrene **1a** to form [1,2-bis(*tert*-butylperoxy)ethyl]benzene **2a** by varying the reagent ratio and the nature of the catalyst. The best results were achieved with $Mn(OAc)_3$ (Table 1).

Table 1 Synthesis of [1,2-bis(*tert*-butylperoxy)ethyl]benzene **2a** from styrene **1a** and *tert*-butyl hydroperoxide using compounds of manganese as catalyst



1a **2a**

Run[a]	Molar ratio **1a** : TBHP : catalyst	Reaction time, h; (solvent)	Yield of **2a**, %
	$Mn(OAc)_3 \bullet 2H_2O$		
1	1 : 4 : 3	48; (CH_3CN)	29
2	1 : 4 : 0.2	48; (CH_3CN)	60
3	1 : 3 : 2	48; (CH_3CN)	42
4	1 : 3 : 0.5	48; (CH_3CN)	58
5	1 : 3 : 0.4	48; (CH_3CN)	70
6	1 : 3 : 0.2	48; (CH_3CN)	73
7[b]	1 : 3 : 0.2	1; (CH_3CN)	46
8	1 : 3 : 0.1	1; (CH_3CN)	7
9	1 : 3 : 0.1	48; (CH_3CN)	75
10	1 : 3 : 0.05	48; (CH_3CN)	53
11	1 : 2 : 0.1	48; (CH_3CN)	60
12	1 : 3 : 0.1	48; (CH_2Cl_2)	16
13	1 : 3 : 0.1	48; (Benzene)	43
14	1 : 3 : 0.1	48; (AcOH)	37
15	1 : 3 : 0.1	48; (Acetone)	57
	MnO_2, $KMnO_4$, $Mn(OAc)_2 \bullet 4H_2O$, $MnCl_2 \bullet 4H_2O$		
16	1 : 3 : 0.1 MnO_2	48; (CH_3CN)	43
17	1 : 3 : 0.3 MnO_2	48; (CH_3CN)	57
18	1 : 3 : 0.4 $KMnO_4$	48; (CH_3CN)	10
19	1 : 3 : 0.1 $Mn(OAc)_2$	48; (CH_3CN)	19
20	1 : 3 : 0.4 $MnCl_2$	72; (CH_3CN)	8

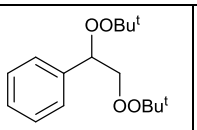
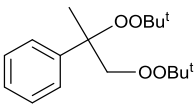
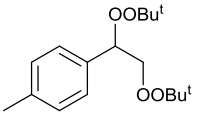
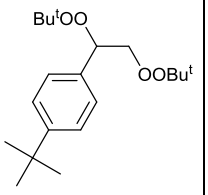
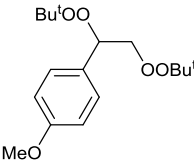
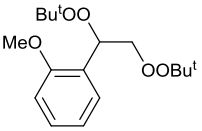
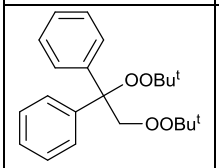
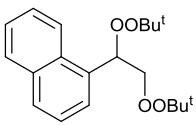
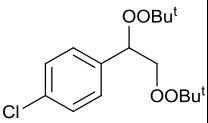
[a] **General procedure:** t-BuOOH and a catalyst were sequentially added with vigorous stirring to a solution of styrene **1a** (0.5 g, 4.85 mmol) in CH_3CN, CH_2Cl_2, benzene, AcOH, acetone (10 mL) at 20-25 °C. 2-Phenyloxirane was obtained in all experiments in yields approximately from 1 to 5 %.

[b] 78-80 °C.

The conditions of the synthesis of peroxide **2a** were optimized mainly with the use of $Mn(OAc)_3$ (runs 1-15), which gave the highest yields of the product, as well as employing MnO_2, $KMnO_4$, $Mn(OAc)_2$, and $MnCl_2$ (runs 16-20). In runs 1-15, the reagent ratio was varied from 2 to 4 moles of TBHP per mole of styrene **1a** and 0.05-3 moles of the catalyst per mole of styrene **1a**. All experiments, except for run 7, were carried out at 20-25 °C. In run 7, at 78-80 °C the reaction time significantly decreased from 48 h to 1 h; however, this led to a substantial decrease in the yield of bisperoxide **2a**. The optimum TBHP/styrene **1a** molar ratio was 3; $Mn(OAc)_3$/styrene **1a** ratio was 0.1-0.4. Application of other solvents CH_2Cl_2, benzene, AcOH, and acetone (runs 12-15) does not permit to increase the yield of **2a.** Supposing that manganese ions in different oxidation states are involved in the formation of bisperoxide **2a**, we carried out experiments 16-20 with the use of MnO_2, $KMnO_4$, $Mn(OAc)_2$, and $MnCl_2$. Despite the difference in the oxidation states of manganese in the compounds used, target bisperoxide **2a** was obtained in these experiments in yields from 8 to 57 %.

In the next step of the study, using the reaction conditions of one of the best experiments (run 9, see Table 1), we performed the synthesis of a number of bisperoxidated ethylarenes **2b-i** (Table 2).

Table 2 Structures and yields of vicinal bisperoxides **2a-i**

 **a** **75%**	 **b** **56%**	 **c** **63%**
 **d** **61%**	 **e** **46%**	 **f** **50%**
 **g** **52%**	 **h** **55%**	 **i** **51%**

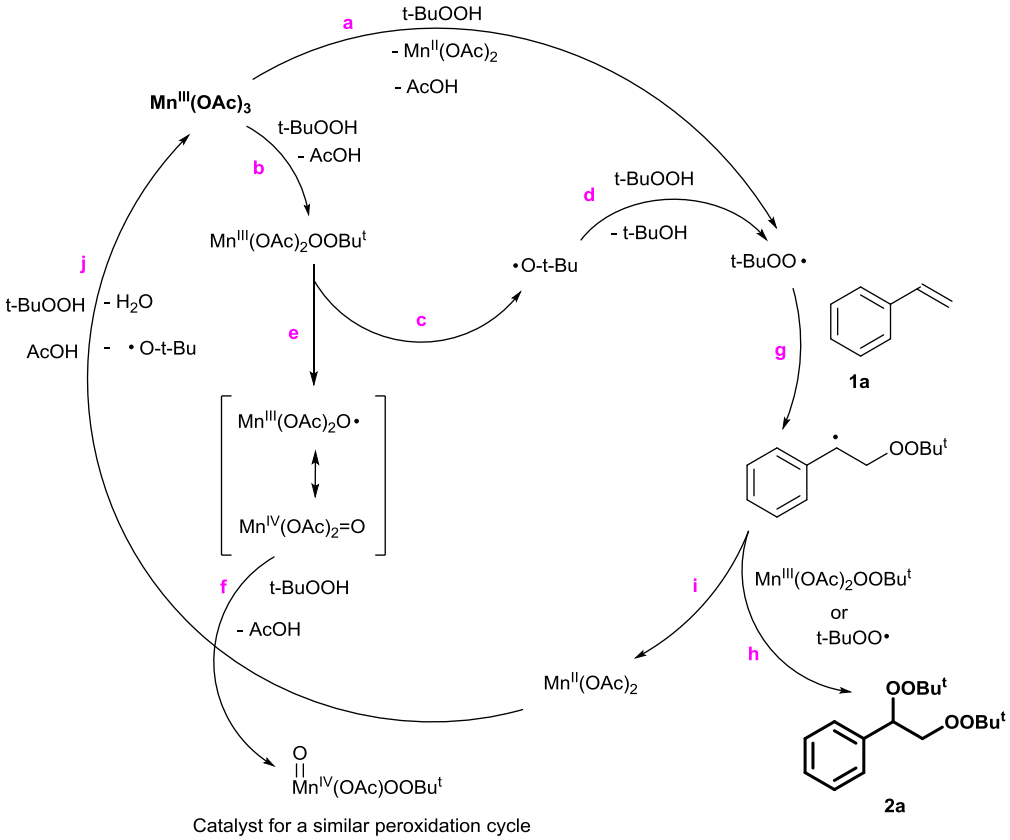
The introduction of a substituent in the aromatic ring or in the vinyl group (at the alpha position) of styrene **1a** has only a slight effect on the formation of bisperoxides. Under the conditions of run 9, bisperoxides **2b-i** were prepared from styrenes **1b-i** in moderate or good yields, which are, however, somewhat lower compared to **2a** (Table 2). These results suggest that other structurally similar styrenes can also be used in the synthesis of the corresponding bisperoxides.

Proposed mechanism of the synthesis of bisperoxides

Based on the results of peroxidation using compounds of manganese in different oxidation states and the literature data on oxidation reactions involving manganese salts,[7,15,20] we proposed the mechanism of the peroxidation (Scheme 2).

In the first step, the reaction of t-BuOOH with $Mn(OAc)_3$ can proceed *via* two pathways (**a** and **b**). In the reaction *via* the pathway **a**, $Mn(OAc)_3$ directly oxidizes t-BuOOH to form the peroxide radical t-BuOO•. In the reaction *via* the pathway **b**, the acetic acid moiety is replaced with *tert*-butyl hydroperoxide to form $Mn^{III}(OAc)_2OO$-t-Bu, which fragments on two particles (arrows **c** and **e**).[7,20] The radical t-BuO• rapidly abstracts hydrogen (step **d**) from t-BuOOH to give t-BuOO•.[21] In the pathway **f**, $Mn^{IV}(OAc)_2{=}O$ is produced from $Mn^{III}(OAc)_2OO$-t-

Bu followed by the reaction of this intermediate with t-BuOOH (similarly to $Mn(OAc)_3$) to form $O{=}Mn^{IV}(OAc)OO\text{-}t\text{-}Bu$.[15]



Scheme 2 Proposed mechanism of the peroxidation of styrene **1a** with *tert*-butyl hydroperoxide using compounds of manganese

Based on the results of the experiment with MnO_2 (runs 16 and 17, Table 1), in which **2a** was obtained in good yield, it can be supposed that $O{=}Mn^{IV}(OAc)OO\text{-}t\text{-}Bu$ initiates a new peroxidation cycle. The radicals t-BuOO• react with styrene **1a** (step **g**) to give the stabilized benzyl radical, which either recombines with t-BuOO• or is oxidized with $Mn^{III}(OAc)_2OO\text{-}t\text{-}Bu$ accompanied by the transfer of the ligand OO-t-Bu (step **h**) to give the target bisperoxide **2a**.[7,15,20] Indirectly existence of benzyl radical is confirmed by the isolation of phenyloxirane which is the product of intramolecular radical substitution of t-BuO•. The compound $Mn(OAc)_2$ that is formed in the steps **a** and **i** is oxidized with t-BuOOH (step **j**) to form $Mn(OAc)_3$. This is how the step-by-step transformation of manganese derivatives in various oxidation states occurs in the catalytic cycle of peroxidation of the C=C bond.

Conclusions

It was shown that manganese salts in oxidation states 2, 3, 4, and 7 catalyze the peroxidation of styrenes with *tert*-butyl hydroperoxide. A method was proposed for the synthesis of [1,2-bis(*tert*-butylperoxy)ethyl]arenes from readily available and cheap starting reagents. Despite a large number of elementary steps in this reaction, the peroxidation is accomplished in moderate or good yields (up to 75%). The synthesized compounds and the method for their preparation may be applied for the production of radical polymerization initiators of unsaturated monomers.

Experimental

Caution: Although we have encountered no difficulties in working with peroxides, precautions, such as the use of shields, fume hoods, and the avoidance of heating and shaking, should be taken whenever possible.

NMR spectra were recorded on a commercial instrument (300.13 MHz for ^1H, 75.48 MHz for ^{13}C) in $CDCl_3$. High resolution mass spectra (HRMS) were measured using electrospray ionization (ESI).[22] The measurements were performed in positive ion mode (interface capillary voltage 4500 V); the mass ratio was from m/z 50 to 3000 Da; external/internal calibration was done with Electrospray Calibrant Solution. A syringe injection was used for solutions in MeCN (flow rate 3 μL/min). Nitrogen was applied as a dry gas; the interface temperature was set at 180 °C.

The TLC analysis was carried out on standard silica gel chromatography plates. Chromatography was performed on silica gel (0.060-0.200 mm, 60 A, CAS 7631-86-9).

Hexane, CH_3CN, benzene, acetone, AcOH, CH_2Cl_2, ethyl acetate (EA), $Mn(OAc)_3{\bullet}2H_2O$, $Mn(OAc)_2{\bullet}4H_2O$, $MnCl_2{\bullet}4H_2O$, MnO_2, and $KMnO_4$ were purchased from Acros.

Experiments for Table 1 (runs 1-11).

In a 15 ml round bottom flask, styrene **1a** (0.5 g, 4.85 mmol) was dissolved in CH_3CN (10 mL). Then a 70% aqueous t-BuOOH

solution (1.25-2.50 g, 9.7-19.4 mmol, 2-4 mol per mole of **1a**) and $Mn(OAc)_3 \bullet 2H_2O$ (0.065-5.2 g, ; 0.243-14.55 mmol, 0.05-3 mol per mole of **1a**) were successively added with stirring. The heterogeneous reaction mixture was stirred at 20-25°C (runs 1-6 and 8-11) for 1 h (run 8) or 48 h (runs 1-6 and 9-11) or at 78-80°C for 1 h (run 7). The reaction mixture was cooled to room temperature (run 7). Then the reaction mixture was extracted with hexane (4×20 mL). The combined organic extracts were concentrated under water aspirator pressure. 1,2-Bis(*tert*-butylperoxy)ethyl]benzene **2a** was isolated by column chromatography on silica gel using ethyl acetate/hexane (5:95, v/v) as the eluent. 2-Phenyloxirane was obtained in all experiments in yields approximately from 1 to 5 %. In the experiment 1 2-phenyloxirane was isolated by column chromatography on silica gel using EA/hexane (5:95, v/v) as the eluent. The yield of 2-phenyloxirane was 5% (0.029 g, 0.24 mmol)

Experiments for Table 1 (runs 12, 13).

In a 15 ml round bottom flask, styrene **1a** (0.5 g, 4.85 mmol) was dissolved in CH_2Cl_2 or benzene (10 mL). Then a 70% aqueous t-BuOOH solution (1.87 g, 14.55 mmol; 3 mol per mole of **1a**) and $Mn(OAc)_3 \bullet 2H_2O$ (0.13 g, 0.485 mmol; 0.1 mol per mole of **1a**) were successively added with stirring. The heterogeneous reaction mixture was stirred at 20-25°C for 48 h. Then the solution was filtered off from manganese salts. The organic phase was concentrated under water aspirator pressure. 1,2-Bis(*tert*-butylperoxy)ethyl]benzene **2a** was isolated by column chromatography on silica gel using EA/hexane (5:95, v/v) as the eluent.

Experiments for Table 1 (run 14, 15).

In a 15 ml round bottom flask, styrene **1a** (0.5 g, 4.85 mmol) was dissolved in AcOH or acetone (10 mL). Then a 70% aqueous t-BuOOH solution (1.87 g, 14.55 mmol; 3 mol per mole of **1a**) and $Mn(OAc)_3 \bullet 2H_2O$ (0.13 g, 0.485 mmol; 0.1 mol per mole of **1a**) were successively added with stirring. The practically homogeneous reaction mixture was stirred at 20-25°C for 48 h. Then $CHCl_3$ (10 mL) and a solution of $Na_2S_2O_3 \cdot 5\ H_2O$ (200 mg) in H_2O (20 mL) were added, the mixture was shaken, the organic layer was separated, and the aqueous layer was extracted with $CHCl_3$ (2×10 mL). Combined organic extracts were successively washed with a saturated aqueous $NaHCO_3$ solution (15 mL) and H_2O (20 mL), and dried under $MgSO_4$. The organic phase was concentrated under water aspirator pressure. 1,2-Bis(*tert*-butylperoxy)ethyl]benzene **2a** was isolated by column chromatography on silica gel using EA/hexane (5:95, v/v) as the eluent.

Experiments for Table 1 (runs 16, 17, 19).

In a 15 ml round bottom flask, styrene **1a** (0.5 g, 4.85 mmol) was dissolved in CH_3CN (10 mL). Then a 70% aqueous t-BuOOH solution (1.87 g, 14.55 mmol, 3 mol per mole of **1a**) and the catalyst $Mn(OAc)_2 \bullet 4H_2O$ or MnO_2 (0.485-1.455 mmol, 0.1-0.3 mol per mole of **1a**) were successively added with stirring. The heterogeneous reaction mixture was stirred at 20-25°C for 48 h. Compound **2a** was isolated as described above (in runs 1-11).

Experiments for Table 1 (runs 18, 20).

In a 15 ml round bottom flask, styrene **1a** (0.5 g, 4.85 mmol) was dissolved in CH_3CN (10 mL). Then a 70% aqueous t-BuOOH solution (1.87 g, 14.55 mmol, 3 mol per mole of **1a**) and the catalyst $MnCl_2 \bullet 4H_2O$ or $KMnO_4$, (1.94 mmol, 0.4 mol per mole of **1a**) were successively added with stirring. In the course of the reaction homogeneous mixture transform to heterogeneous. The mixture was stirred at 20-25°C for 48 h (in run 20 for 72 h). Compound **2a** was isolated as described above (in run 14,15).

Experiments for Table 2. Synthesis of bisperoxides 2b-i.

In a 15 ml round bottom flask, compound **1b-1i** (0.573-0.873 g, 4.85 mmol) was dissolved in CH_3CN (10 mL). Then a 70% aqueous t-BuOOH solution (1.87 g, 14.55 mmol; 3 mol per mole of **1b-1i**) and $Mn(OAc)_3 \bullet 2H_2O$ (0.13 g, 0.485 mmol; 0.1 mol per mole of **1b-1i**) were successively added with stirring. The heterogeneous reaction mixture was stirred at 20-25°C for 48 h. Compounds **2b-i** were isolated as described for **2a**.

[1,2-Bis(*tert*-butylperoxy)ethyl]benzene, 2a[12,15]

Colourless oil; R_f = 0.77 (ethyl acetate/hexane = 5:95); ^{1}H NMR (300.13 MHz, $CDCl_3$): δ 1.26 (s, 9H, t-BuOO), 1.27 (s, 9H, t-BuOO), 4.09 (dd, *J* = 11.5, 4.0 Hz, 1H, CH_2), 4.25 (dd, *J* = 11.5, 7.6 Hz, 1H, CH_2), 5.23 (dd, *J* = 7.6, 4.0 Hz, 1H, CH), 7.25-7.43 (m, 5H, ArH); ^{13}C NMR (75.48 MHz, $CDCl_3$): δ 26.3, 26.4, 76.8, 80.4, 80.5, 83.3, 127.0, 127.9, 128.2, 138.6; Anal. calcd. for $C_{16}H_{26}O_4$: C 68.06, H 9.28; found: C 68.10, H 9.22; HRMS (ESI) calcd. for $C_{16}H_{26}NaO_4$ [M+Na$^+$]: 305.1723, found: 305.1720.

[1,2-Bis(*tert*-butylperoxy)-1-methylethyl]benzene, 2b[14,15]

Colourless oil; R_f = 0.82 (ethyl acetate/hexane = 5:95); ^{1}H NMR (300.13 MHz, $CDCl_3$): δ 1.21 (s, 9H, t-BuOO), 1.26 (s, 9H, t-BuOO), 1.67 (s, 3H, CH_3), 4.25 (m, 2H, CH_2O), 7.24-7.55 (m, 5H, ArH); ^{13}C NMR (75.48 MHz, $CDCl_3$): δ 21.9, 26.3, 26.6, 79.2, 79.4, 80.5, 82.9, 126.1, 127.1, 127.8, 143.0; Anal. calcd. for $C_{17}H_{28}O_4$: C 68.89, H 9.52; found: C 69.12, H 9.74; HRMS (ESI) calcd. for $C_{17}H_{28}NaO_4$ [M+Na$^+$]: 319.1880, found: 319.1876.

1-[1,2-Bis(*tert*-butylperoxy)ethyl]-4-methylbenzene, 2c

Colourless oil; R_f = 0.75 (ethyl acetate/hexane = 5:95); ^{1}H NMR (300.13 MHz, $CDCl_3$): δ 1.25 (s, 9H, t-BuOO), 1.26 (s, 9H, t-BuOO), 2.36 (s, 3H, CH_3), 4.08 (dd, *J* = 11.4, 4.0 Hz, 1H, CH_2), 4.25 (dd, *J* = 11.4, 7.7 Hz, 1H, CH_2), 5.19 (dd, *J* = 7.7, 4.0 Hz, 1H, CH), 7.17 (d, *J* = 8.1 Hz, ArH), 7.27 (d, *J* = 8.1 Hz, ArH); ^{13}C NMR (75.48 MHz, $CDCl_3$): δ 21.2, 26.3, 26.4, 76.8, 80.4, 80.6, 83.2, 127.0, 128.9, 135.5, 137.6; Anal. calcd. for $C_{17}H_{28}O_4$: C 68.89, H 9.52; found: C 69.24, H 9.60; HRMS (ESI) calcd. for $C_{17}H_{32}NO_4$ [M+NH_4^+]: 314.2326, found: 314.2324.

1-[1,2-Bis(*tert*-butylperoxy)ethyl]-4-*tert*-butylbenzene, 2d

Colourless oil; R_f = 0.8 (ethyl acetate/hexane = 5:95); ^{1}H NMR (300.13 MHz, $CDCl_3$): δ 1.25 (s, 9H, t-BuOO), 1.27 (s, 9H, t-BuOO), 1.32 (s, 9H, t-BuOO), 4.09 (dd, *J* = 11.4, 4.0 Hz, 1H, CH_2), 4.25 (dd, *J* = 11.4, 7.7 Hz, 1H, CH_2), 5.20 (dd, *J* = 7.7, 4.0 Hz, 1H), 7.30 (d, *J* = 8.1 Hz, ArH), 7.37 (d, *J* = 8.1 Hz, ArH); ^{13}C NMR (75.48 MHz, $CDCl_3$): δ 26.3, 26.4, 31.3, 34.5, 76.9, 80.4, 80.6, 83.2, 125.2, 126.7, 135.5, 150.7; Anal. calcd. for $C_{20}H_{34}O_4$: C 70.97, H 10.12; found: C 70.99, H 10.15; HRMS (ESI) calcd.

for $C_{20}H_{34}NaO_4$ [M+Na^+]: 361.2349, found: 361.2335.

1-[1,2-Bis(*tert*-butylperoxy)ethyl]-4-methoxybenzene, 2e

Colourless oil; R_f = 0.51 (ethyl acetate/hexane = 5:95); ^{1}H NMR (300.13 MHz, $CDCl_3$): δ 1.24 (s, 9H, t-BuOO), 1.25 (s, 9H, t-BuOO), 3.81 (s, 3H, CH_3O), 4.08 (dd, *J* = 11.4, 4.3 Hz, 1H, CH_2), 4.26 (dd, *J* = 11.4, 7.5 Hz, 1H, CH_2), 5.15 (dd, *J* = 7.5, 4.3 Hz, 1H, CH), 6.89 (d, *J* = 8.6 Hz, 2H, ArH), 7.29 (d, *J* = 8.6 Hz, 2H, ArH); ^{13}C NMR (75.48 MHz, $CDCl_3$): δ 26.3, 26.4, 55.2, 76.7, 80.4, 80.5, 82.8, 113.7, 128.4, 130.7, 159.4; Anal. calcd. for $C_{17}H_{28}O_5$: C 65.36, H 9.03; found: C 65.41, H 9.07; HRMS (ESI) calcd. for $C_{17}H_{32}NO_5$ [M+NH_4^+]: 330.2275, found: 330.2275.

1-[1,2-Bis(*tert*-butylperoxy)ethyl]-2-methoxybenzene, 2f

Colourless oil; R_f = 0.55 (ethyl acetate/hexane = 5:95); ^{1}H NMR (300.13 MHz, $CDCl_3$): δ 1.26 (s, 9H, t-BuOO), 1.28 (s, 9H, t-BuOO), 3.83 (s, 3H, OCH_3), 4.08 (dd, *J* = 11.1, 7.9 Hz, 1H, CH_2), 4.17 (dd, *J* = 11.1, 3.1 Hz, 1H, CH_2), 5.60 (dd, *J* = 11.1, 7.9 Hz, 1H, CH), 6.84-6.89 (m, 1H, ArH), 6.94-7.01 (m, 1H, ArH), 7.23-7.29 (m, 1H, ArH), 7.44-7.48 (m, 1H, ArH); ^{13}C NMR (75.48 MHz, $CDCl_3$): δ 26.3, 26.4, 55.3, 76.0, 78.8, 80.4, 80.6, 110.4, 120.4, 126.7, 127.8, 128.7, 156.7; Anal. calcd. for $C_{17}H_{28}O_5$: C 65.36, H 9.03; found: C 65.31, H 9.11; HRMS (ESI) calcd. for $C_{17}H_{32}NO_5$ [M+NH_4^+]: 330.2275, found: 330.2277.

[1,2-Bis(*tert*-butylperoxy)-1-phenylethyl]benzene, 2g[14]

Colourless oil; R_f = 0.71 (ethyl acetate/hexane = 5:95); ^{1}H NMR (300.13 MHz, $CDCl_3$): δ 1.11 (s, 9H, t-BuOO), 1.23 (s, 9H, t-BuOO), 4.83 (s, 2H, CH_2), 7.23-7.35 (m, 10H, ArH); ^{13}C NMR (75.48 MHz, $CDCl_3$): δ 26.3, 26.6, 77.6, 79.6, 80.5, 85.7, 127.3, 127.5, 127.8, 142.1; Anal. calcd. for $C_{22}H_{30}O_4$: C 73.71, H 8.44; found: C 73.69, H 8.50; HRMS (ESI) calcd. for $C_{22}H_{30}NaO_4$ [M+Na^+]: 381.2036, found: 381.2031.

1-[1,2-Bis(*tert*-butylperoxy)ethyl]naphthalene, 2h

Colourless oil; R_f = 0.77 (ethyl acetate/hexane = 5:95); ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 1.31 (s, 9H, t-BuOO), 1.34 (s, 9H, t-BuOO), 4.22-4.33 (m, 2H, CH_2), 6.08-6.15 (m, 1H, CH), 7.46-7.59 (m, 3H, ArH), 7.69-7.76 (m, 1H, ArH), 7.78-7.93 (m, 2H, ArH), 8.18-8.24 (m, 1H, ArH); ^{13}C NMR (75.48 MHz, $CDCl_3$): δ 26.3, 26.5, 77.0, 80.5, 80.7, 80.8, 123.2, 124.4, 125.4, 126.0, 128.2, 128.8, 130.9, 133.8, 134.2; Anal. calcd. for $C_{20}H_{28}O_4$: C 72.26, H 8.49; found: C 72.38, H 8.30; HRMS (ESI) calcd. for $C_{20}H_{28}NaO_4$ [M+Na^+]: 355.1880, found: 355.1869.

1-[1,2-Bis(*tert*-butylperoxy)ethyl]-4-chlorobenzene, 2i

Colourless oil; R_f = 0.69 (ethyl acetate/hexane = 5:95); ^{1}H NMR (300.13 MHz, $CDCl_3$): δ 1.23 (s, 9H, t-BuOO), 1.24 (s, 9H, t-BuOO), 4.03 (dd, *J* = 11.7, 4.2 Hz, 1H, CH_2), 4.19 (dd, *J* = 11.7, 7.5 Hz, 1H, CH_2), 5.19 (dd, *J* = 7.5, 4.2 Hz, 1H, CH), 7.26-7.35 (m, ArH); ^{13}C NMR (75.48 MHz, $CDCl_3$): δ 26.2, 26.3, 76.4, 80.5, 80.7, 82.6, 128.4, 128.5, 133.6, 137.2; anal. calcd. for $C_{16}H_{25}ClO_4$: C 60.66, H 7.95, Cl 11.19, found: C 60.44, H 7.62, Cl 11.20; HRMS (ESI) calcd. for $C_{16}H_{29}ClNO_4$ [M+NH_4^+]: 334.1780, found: 334.1774.

2-Phenyloxirane

Colourless oil; R_f = 0.39 (ethyl acetate/hexane = 5:95); ^{1}H NMR (300.13 MHz, $CDCl_3$): δ 2.82 (dd, *J* = 5.50, 2.57 Hz, 1H, CH_2), 3.16 (dd, *J* = 5.50, 4.04 Hz, 1H, CH_2), 3.88 (dd, *J* = 4.04, 2.57 Hz, 1H, CH), 7.23-7.45 (m, ArH); ^{13}C NMR (75.48 MHz, $CDCl_3$): δ 51.1, 52.2, 125.4, 128.1, 128.4, 137.6.

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