

Preparation of New Substituted Bis(benzoyl) Peroxides under Aqueous Conditions in the Presence of Stearyltrimethylammonium Chloride

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Summary. A series of new substituted bis(benzoyl) peroxides has been synthesised from their corresponding acid chlorides in high yield. The reactions were carried out in aqueous sodium peroxide solution and butanone in the presence of 0.5% stearyltrimethylammonium chloride (*STAC*) at a temperature below 15°C. *STAC* improved the purity, and the fast addition improved the yield of the peroxides. Mass spectral analysis of substituted bis(benzoyl) peroxides using EI has been carried out for accurate mass determinations.

Keywords. Bis(*p*-alkylbenzoyl) peroxide; Bis(*p*-*n*-decylbenzoyl) peroxide; Bis(*p*-alkoxybenzoyl) peroxide; Bis(*p*-*n*-butoxybenzoyl) peroxide; Stearyltrimethylammonium chloride.

Introduction

Benzoyl peroxides are widely used for the initiation of free radical polymerisations and in grafting reactions to form copolymers. Their solubility in the reaction medium (solvent, monomers, molten polymer) can be altered by introducing substituents on the aryl rings and this can affect the course of the polymerisation reactions. To systematically study the effect of different alkyl substituents of the benzoyl peroxides, we required efficient synthetic procedures to prepare these compounds. This paper describes the synthesis of new substituted bis(benzoyl) peroxides by an adaptation of known methods [1].

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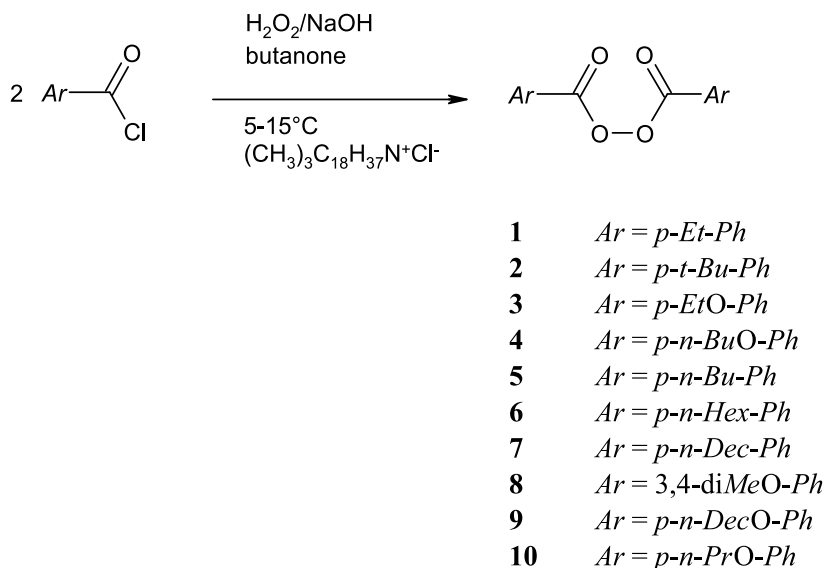
Results and Discussion

Synthesis

Stearyltrimethylammonium chloride (*STAC*) was added to a little water and then heated to 55°C to form a micellar solution. This solution was cooled to room temperature.

A substituted benzoyl chloride in butanone was added dropwise to an aqueous premixed solution of hydrogen peroxide and sodium hydroxide in the presence of 0.5 to 1 wt% *STAC* as a surfactant [2, 3]. The temperature was kept below 15°C. (Scheme 1).

For comparative and reference purposes three known substituted bis(benzoyl) peroxides, namely bis(*p*-ethylbenzoyl)- (**1**), bis(*p*-*t*-butylbenzoyl)- (**2**), and bis(*p*-ethoxybenzoyl) peroxide (**3**), were included in the study. We found that **1**, **2**, and bis(*p*-*n*-butoxybenzoyl) peroxide (**4**) formed solid precipitates during the addition. Without surfactant it became obvious that some substituted bis(benzoyl) peroxides, namely **2** and **4**, formed unwanted lumps during the addition. When these bis(benzoyl) peroxides were analysed, they were found to contain up to 30% of the corresponding substituted benzoic acids as coprecipitated impurities. With *STAC* as a surfactant, substituted bis(benzoyl) peroxides, for example **1**, and especially those substituted bis(benzoyl) peroxides with longer alkyl groups like bis(*p*-*n*-butylbenzoyl)- (**5**), bis(*p*-*n*-hexylbenzoyl)- (**6**), and bis(*p*-*n*-decylbenzoyl) peroxide (**7**) did not precipitate during the addition. These peroxides, when using more butanone, remained in the butanone layer on top of the aqueous layer. Evaporation of the butanone layer produced a solid crust of the peroxide with *little or no water present* (**CAUTION**). In the case of **6** a precipitate only formed when all the butanone had evaporated; the resulting compound had a low melting point. Anhydrous **5** and **7** are solids when pure, but they remained oils at room temperature



Scheme 1

when they contain only little impurities. Peroxides **5** and **7** were better isolated by extraction from the water layer. This was first cautiously tried with **5** by extraction with petroleum ether (bp = 30–40°C). After evaporation of the solvent, the product obtained was surfactant free almost 100% pure **5** with no water (**CAUTION**). Bis(*p*-*n*-decylbenzoyl) peroxide (**7**) could not be extracted with petroleum ether and ethyl acetate was used instead. Again, no *STAC* was found in the final product. Less soluble sodium benzoyl peroxides and substituted benzoic acids remained in the surfactant aqueous solution and gave the water layer a milky to translucent appearance. When the peroxides were isolated as water-free oils, they usually solidified at room temperature to form waxes. **Extreme caution should be observed in handling these materials.** This method is therefore not recommended for peroxide isolation.

The active oxygen contents of **5**, **6**, and **7** are 4.5, 3.9, and 3.1 wt% compared to bis(benzoyl) peroxide with an active oxygen content of 6.6 wt%. This makes **7** a fairly safe material, even in pure form without water. Last mentioned three bis(benzoyl) peroxides were purified by recrystallisation from petroleum ether (bp = 40–60°C) by dissolving these compounds at room temperature and then cooling the solution to –10°C. In general, the peroxide reaction of substituted benzoyl chlorides with long aliphatic chains (*R* = *p*-*n*-hexyl-, *p*-*n*-decyl-) occurred at a much slower rate and a 24 hour reaction period was required. By comparison, the bis(alkoxybenzoyl) peroxides formed very rapidly. A 100 gram batch of *p*-ethoxybenzoyl chloride was transformed to the desired **3** in less than 30 minutes. Furthermore, increasing the amount of butanone in the reaction mixture either during or before the addition of the acid chloride, also curbed lumping and improved the purity of the precipitated peroxide. Adding an additional amount of butanone *after* the addition improved the purity and yield of certain bis(benzoyl) peroxides that form more slowly, *e.g.* **6** and **7**.

Reducing the excess amount of sodium hydroxide required, minimized cleavage of the bis(benzoyl) peroxide. Thus, instead of 15–20% excess NaOH, only ~5% excess NaOH were used. The hydrogen peroxide excess, on the other hand, was increased from just 10% to up to 50% (and in some cases twice the amount) and had no adverse effect on the bis(benzoyl) peroxide purity, provided that the temperature was kept below 15°C. More importantly, the concentration of hydrogen peroxide was not always reliable. It seemed that excess hydrogen peroxide did not make the reaction more hazardous by forming butanone peroxides since these peroxides either stayed in the aqueous layer or as liquids in ketone solvents and did not coprecipitate with the solid bis(benzoyl) peroxides (NMR). With some bis(benzoyl) peroxide preparations, for example bis(3,4-dimethoxybenzoyl) peroxide (**8**) and bis(*n*-decyloxybenzoyl) peroxide (**9**), the reaction did not go to completion. In such cases the hydrolyses of the acid chloride competed with peroxide formation and for these compounds low yields were obtained. The corresponding substituted benzoic acid and an equal amount of HCl had formed. The final reaction mixture reached an acidity level well below *pH* = 2. Where this problem was severe, we have found that it was best to work up the reaction immediately to curb acid catalysed cleavage of the peroxide. Therefore, thirty minutes after the addition of the acid chloride to the sodium peroxide solution had completed, excess sodium hydrogencarbonate was added to the mixture to neutralise the aqueous solution.

It was important though to do this addition in small portions, because the CO₂ that was released caused a foam due to the surfactant.

Analysis of Substituted Bis(benzoyl) Peroxides

Bis(*p*-alkylbenzoyl) peroxides with long aliphatic chains (namely **5**, **6**, and **7**, Scheme 1) were all soluble and recrystallised from cold petroleum ether (bp = 40–60°C) but were less soluble in methanol. However, the bis(alkoxybenzoyl) peroxides were soluble in chloroform, but methanol was important to use as a co-solvent in the recrystallisations to trap excessive amounts of water. Bis(*p*-ethoxybenzoyl) peroxide (**3**) had the lowest solubility and was purified by recrystallisation from methanol, but this peroxide could also be recrystallised from chloroform.

The determination of the melting points of anhydrous bis(benzoyl) peroxides was carried out on very small samples using a heating block and visually monitored by optical microscopy rather than a melting tube. Peroxides **2** and **3** decomposed before their melting points were reached, this was typically observed as a slow fizz, due to the evolution of CO₂ and with some liquification or solidification.

Experimental

Note: Peroxides are shock-sensitive and therefore hazardous and need to be handled with appropriate care. Peroxide preparations should be carried out in a fumehood behind a safety shield.

The reaction of the substituted benzoic acids with thionyl chloride was carried out at 90°C for 4 h. The process was followed visually. At room temperature the white paste of the mixture of the substituted benzoic acid and thionyl chloride reacted very slowly. Above 60°C a fast evolution of HCl and SO₂ occurred with the gradual disappearance of the white solid. No noticeable cleavage of the alkoxy group occurred during the formation of the acid chloride and no obvious formation of the anhydride was found. High-vacuum distillation was included as a necessary purification step for the preparation of all distillable substituted benzoyl chlorides. *p*-*n*-Decoxybenzoyl chloride could not easily be distilled and was therefore impure, as a result bis(*p*-*n*-decoxybenzoyl) peroxide, which was prepared, was also very impure. A 13 wt% stock solution of STAC was prepared at 55°C and

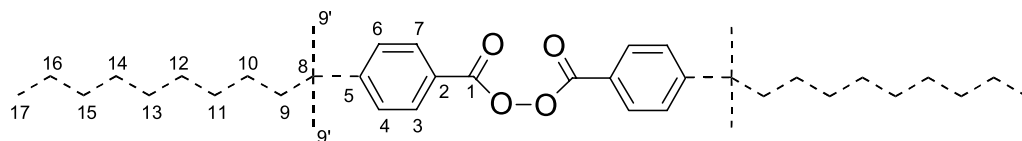


Fig. 1. Numbering used of compounds **2**, **5**, **6**, and **7** for spectrometric assignments

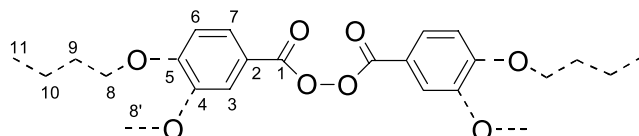


Fig. 2. Numbering used of compounds **3**, **4**, **8**, and **10** for spectrometric assignments

cooled to room temperature before addition. Butanone was not redistilled. **As a safety precaution it was important to obtain at least a 20 wt% moisture content in the free-flowing peroxide powder.**

^1H and ^{13}C NMR of bis(benzoyl) peroxides were run on a Varian Gemini instrument at 200 and 50 MHz. For aromatic coupling constants, $J_o = 8.8\text{--}9.0\text{ Hz}$, $J_m = \sim 1\text{--}2\text{ Hz}$. For aliphatic coupling constants $J = 6.9\text{--}7.1\text{ Hz}$. The NMR analyses of the moisture content was carried out only 24 h after precipitation of the peroxide and was determined in acetone- d_6 . However, with some compounds it was necessary to add CDCl_3 or $\text{DMSO-}d_6$ to the deuterated solvents to facilitate dissolution. For example, **7** was poorly soluble in acetone and some CDCl_3 had to be added in such an amount that all H_2O was still dissolved in the deuterated solvent mixture. The mass spectra were obtained with a ThermoQuest MAT95XL high resolution mass spectrometer in the EI mode at a source temperature of 200°C and a source pressure of 5.10^{-6} mbar. Substituted bis(benzoyl) peroxides were dissolved in acetonitrile and introduced *via* a direct insertion probe. The source probe was ramped from room temperature until sufficient to vaporise the sample. Previously, mass spectra of bis(benzoyl) peroxide and bis(*p*-toluoyl) peroxide have been measured using methane chemical ionisation (CI) [5]. To the best of our knowledge, this is the first time that mass spectra of pure bis(benzoyl) peroxides have been determined utilising electron impact (EI) for accurate mass determinations of molecular ions [6]. IR of 14 asymmetric- and symmetric sulfo-substituted bis(benzoyl) peroxides (*p*- $\text{RSO}_2\text{C}_6\text{H}_4(\text{CO})\text{OOCOPh}$) have been reported and were determined at $\bar{\nu} = 1790$ (C=O), 1770 (C=O), 1230 (C–O–), and 1000 cm^{-1} (C–O–O–C) [7].

*Bis(4-*t*-butylbenzoyl) Peroxide (2, [4])*

A 60.0 g of 30 wt% aqueous H_2O_2 (529 mmol) in 65 cm^3 of H_2O solution was added within 20 min to a 50.0 g of 30 wt% aqueous NaOH (375 mmol) in 100 cm^3 of H_2O solution at -5°C . A 13 wt% solution of STAC (10 cm^3) was added to the reaction mixture. A solution of 65.0 g of *p*-*t*-butylbenzoyl chloride (331 mmol) in 40 cm^3 of butanone was added to the reaction mixture within 30 min at 5°C . Then, 600 cm^3 of H_2O were added followed by 10 g of NaHCO_3 . The white precipitate was collected by filtration and washed with deionised H_2O to give 93.17 g of wet **2** (38 wt% H_2O). Yield of active compound: 57.9 g (99%). Recrystallisation from petroleum ether:chloroform (1:1). Mp $133\text{--}138^\circ\text{C}$ (dec) (Ref. [4] $142\text{--}143^\circ\text{C}$); $t_{1/2}$ (10 h) = 68.3°C ; HRMS (CI): $m/z = \text{calcd. for } \text{C}_{22}\text{H}_{26}\text{O}_4 (\text{M}^+) 354.18311$, found 354.1830; IR: $\bar{\nu} = 3080\text{ w}$, 2962 s , 2885 s , 1785 m , 1759 s , 1607 s , 1572 w , 1464 m , 1412 s , 1366 m , 1249 s , 1220 s , 1178 s , 1108 m , 1030 s , 992 s , 908 s , 850 m , 765 m , 734 s , 700 m cm^{-1} ; ^1H NMR (CDCl_3): $\delta = 8.04$ (d, $J = 9\text{ Hz}$, H-3, H-7), 7.55 (d, $J = 9\text{ Hz}$, H-4, H-6), 1.37 (s, H-9) ppm; ^{13}C NMR (CDCl_3): $\delta = 163.09$ (C-1), 122.78 (C-2), 129.69 (C-3, C-7), 125.83 (C-4, C-6), 158.11 (C-5), 35.26 (C-8), 31.02 (C-9) ppm.

Bis(p-ethoxybenzoyl) Peroxide (3, [4])

A 75.0 g of 30 wt% aqueous H_2O_2 (662 mmol) in 100 cm^3 of H_2O solution was added to a 60.0 g of 30 wt% aqueous NaOH (450 mmol) solution at -5°C within 20 min. At first, a very exothermic reaction occurred (rapid increase in temperature, **CAUTION**) with the simultaneous formation of a white paste which then became transparent after final addition. The reaction mixture was not allowed to rise above 15°C . The mixture was stirred for a further 20 min and then cooled to 5°C . A 13 wt% solution of STAC (10 cm^3) was added to the mixture to suppress lump formation during the peroxide formation. A solution of 70.0 g of *p*-ethoxybenzoyl chloride (379.1 mmol) in 40 cm^3 of butanone was slowly added to the cooled aqueous sodium peroxide solution within 45 min under stirring whereby the temperature rose to 15°C . Halfway through the addition, 130 cm^3 of butanone were added to the reaction mixture to facilitate stirring. The temperature was kept $< 15^\circ\text{C}$ for another 2 h. 3.0 g of NaHCO_3 (0.0357 mol) were added to the reaction mixture to raise the *pH* to ~ 7 . The mixture was

then diluted with H₂O to a volume of 1 dm³ to enhanced the peroxide precipitation and the mixture was kept for 16 h at 4°C. The fine white suspension was filtered and the product was washed with water to give 81.9 g of free flowing but wet **3** (46 wt% H₂O). Yield of active compound: 44.5 g (71%). Mp 137–139°C (dec) (Ref. [4] 131–132°C) $t_{1/2}$ (10 h) = 40.5°C; HRMS (CI): m/z = calcd. for C₁₈H₁₈O₆ (M⁺) 330.11034, found 330.1106; IR: $\bar{\nu}$ = 3090 w, 2992 m, 2960 m, 2930 w, 2890 w, 1780 s, 1753 s, 1606 s, 1577 m, 1508 m, 1459 m, 1427 m, 1390 m, 1311 m, 1275 s, 1237 s, 1169 m, 1123 m, 1045 s, 991 m, 908 s, 843 m, 738 s cm⁻¹; ¹H NMR (CDCl₃): δ = 7.95 (d, J = 9 Hz, H-3, H-7), 7.03 (d, J = 9 Hz, H-4, H-6), 4.12 (q, J = 7 Hz, H-8), 1.40 (t, J = 7 Hz, H-9) ppm; ¹³C NMR (CDCl₃): δ = 162.33 (C-1), 115.40 (C-2), 130.16 (C-3, C-7), 113.33 (C-4, C-6), 161.01 (C-5), 62.34 (C-8), 12.94 (C-9) ppm.

Bis(p-n-butoxybenzoyl) Peroxide (4, C₂₂H₂₆O₆)

A 6.5 g of 30 wt% aqueous H₂O₂ (57.33 mmol) in 25 cm³ of H₂O solution was added to a 15.0 g of 30 wt% aqueous NaOH (112.5 mmol) solution at –5°C within 15 min and the mixture was stirred for a further 20 min. The temperature was not allowed to rise above 10°C. A 13 wt% solution of STAC (5 cm³) was added to the sodium peroxide at 5°C. Then, a solution of 20.0 g of *p-n*-butoxybenzoyl chloride (94.04 mmol) in 5 cm³ of butanone was added within 30 min to the cooled reaction mixture at 3°C under stirring whereby the temperature rose to 7°C. The reaction mixture became a white paste and was then treated with 35 cm³ of butanone and stirred at room temperature. H₂O (500 cm³) was added to the reaction mixture to complete precipitation. The precipitate was filtered and washed with 250 cm³ of deionised water to give 24.65 g of wet **4** (28 wt% H₂O, 8% impurity due to *p-n*-butoxybenzoic acid). Yield of active compound: 16.46 g (91%). Recrystallisation from petroleum ether: chloroform (1:1). Mp 110.5°C; $t_{1/2}$ (10 h) = 37.5°C; HRMS (CI): m/z = calcd. for C₂₂H₂₆O₆ (M⁺) 386.17294, found 386.1724; IR: $\bar{\nu}$ = 2963 s, 2930 m, 2880 w, 1780 s, 1753 s, 1606 s, 1577 w, 1510 m, 1467 w, 1315 w, 1255 m, 1235 s, 1168 s, 1019 m, 993 m, 909 s, 843 w, 732 s, 650 w cm⁻¹; ¹H NMR (CDCl₃): δ = 8.02 (d, J = 9 Hz, H-3, H-7), 6.96 (d, J = 9 Hz, H-4, H-6), 4.04 (d, J = 7 Hz, H-8), 1.81 (t, J = 7 Hz, H-9), 1.51 (hex, J = 7 Hz, H-10), 0.99 (t, J = 7 Hz, H-11) ppm; ¹³C NMR (CDCl₃): δ = 163.93 (C-1), 117.31 (C-2), 131.91 (C-3, C-7), 114.57 (C-4, C-6), 162.98 (C-5), 68.03 (C-8), 31.04 (C-9), 19.15 (C-10), 13.78 (C-11) ppm.

Bis(p-n-butylbenzoyl) Peroxide (5, C₂₂H₂₆O₄)

A 20 g of 30 wt% aqueous H₂O₂ (176.5 mmol) in 25 cm³ of H₂O solution was added slowly to a 40 g of 30 wt% aqueous NaOH (300 mmol) solution at –5°C within 15 min and the mixture was stirred for a further 30 min. The temperature was not allowed to rise above 10°C. Butanone (25 cm³) followed by a 10 cm³ of 13 wt% solution of STAC was added to the sodium peroxide. A solution of 54.54 g of *p-n*-butylbenzoyl chloride (277.3 mmol) in 25 cm³ of butanone was added within 30 min to the cooled reaction mixture at ~5°C. No precipitation was observed and the reaction mixture separated into two layers. H₂O (500 cm³) was added to the stirred reaction mixture. A viscous oil floated to the top of the beaker and was left in a draft of the fume hood. No crust developed and the oil was separated to give nearly 40.08 g of anhydrous **5** (3 wt% H₂O, **CAUTION**). This oil solidified on standing at room temperature (**CAUTION**). Yield of active compound: 39.1 g (80%). This compound was recrystallised from cold petroleum ether. Mp 30.4°C; $t_{1/2}$ (10 h) = 71.7°C; HRMS (CI): m/z = calcd. for C₂₂H₂₆O₄ (M⁺) 354.18311, found 354.1829; IR: $\bar{\nu}$ = 3080 w, 3040 w, 2960 s, 2933 s, 2863 s, 1795 s, 1764 s, 1691 m, 1610 s, 1574 w, 1466 m, 1417 m, 1229 s, 1178 s, 1028 m, 994 s, 909 m, 846 m, 734 s cm⁻¹; ¹H NMR (CDCl₃): δ = 7.99 (d, J = 9 Hz, H-3, H-7), 7.32 (d, J = 9 Hz, H-4, H-6), 2.70 (t, J = 6 Hz, H-8), 1.64 (m, H-9), 1.37 (H, J = 6 Hz, H-10), 0.95 (t, J = 6 Hz, H-11) ppm; ¹³C NMR (CDCl₃): δ = 163.17 (C-1), 122.94 (C-2), 129.82 (C-3, C-7), 128.89 (C-4, C-6), 150.11 (C-5), 35.81 (C-8), 33.14 (C-9), 22.27 (C-10), 13.87 (C-11) ppm.

Bis(p-n-hexylbenzoyl) Peroxide (6, C₂₆H₃₄O₄)

A 7.5 g of 30 wt% aqueous H₂O₂ (66.15 mmol) in 25 cm³ of H₂O solution was added slowly to a 17.0 g of 30 wt% aqueous NaOH (127.5 mmol) solution at 5°C within 25 min and the mixture was stirred for a further 20 min. The temperature was not allowed to rise above 10°C. Butanone (25 cm³) followed by a 10 cm³ of 13 wt% solution of STAC was added to the sodium peroxide solution and the reaction mixture was cooled to 5°C. A solution of 25.0 g of *p-n*-hexylbenzoyl chloride (111.2 mmol) in 25 cm³ of butanone was added within 30 min to the cooled reaction mixture at 5°C and the mixture was stirred overnight at room temperature. Then, 500 cm³ of H₂O were added to the reaction mixture. Extraction with 2 × 400 cm³ of EtOAc followed by washing the organic extract with 2 × 100 cm³ of H₂O gave, after drying with MgSO₄ and solvent evaporation on a cold rotavaporator (**CAUTION**), 24.3 g of **6** as an oil (4 wt% H₂O, 4 wt% impurity). Yield of active compound: 22.3 g (98%). Product **6** was recrystallised from cold petroleum ether. Mp 38.3°C; *t*_{1/2} (10 h) = 72.6°C; HRMS (CI): *m/z* = calcd. for C₂₆H₃₄O₄ (M⁺) 410.24571, found 410.2457; IR: $\bar{\nu}$ = 2965 m, 2932 s, 2885 m, 1795 m, 1764 s, 1686 s, 1610 m, 1465 w, 1420 m, 1289 m, 1229 s, 1178 m, 1029 s, 995 s, 858 w, 755 w cm⁻¹; ¹H NMR (CDCl₃): δ = 7.99 (d, *J* = 9 Hz, H-3, H-7), 7.32 (d, *J* = 9 Hz, H-3, H-7), 2.69 (t, *J* = 6 Hz, H-8), 1.65 (m, H-9), 1.32 (m, H-10–H-12), 0.89 (t, *J* = 6 Hz, H-13) ppm; ¹³C NMR (CDCl₃): δ = 163.19 (C-1), 122.94 (C-2), 129.82 (C-3, C-7), 128.88 (C-4, C-6), 150.14 (C-5), 36.12 (C-8), 31.61 and 30.99 (C-9 and/or C-10), 28.85 (C-11), 22.54 (C-12), 14.04 (C-13) ppm.

Bis(p-n-decylbenzoyl) Peroxide (7, C₃₄H₅₀O₄)

A 14.0 g of 30 wt% aqueous H₂O₂ (123.5 mmol) in 50 cm³ of H₂O solution was added within 15 min to a 25.0 g of 30 wt% aqueous NaOH (188 mmol) solution at 0°C and then stirred for a further 20 min. The temperature was not allowed to rise above 15°C. Butanone (25 cm³) was added to the aqueous sodium peroxide solution followed by a 10 cm³ of 13 wt% solution of STAC. A solution of 50.0 g of *p-n*-decylbenzoyl chloride (178 mmol) in 25 cm³ of butanone was then added within 30 min to the cooled sodium peroxide solution at 5°C and the mixture was stirred for 15 h at room temperature. H₂O (500 cm³) was added to the reaction mixture to facilitate workup. Extraction with 2 × 400 cm³ of EtOAc followed by washing of the organic extract with 2 × 100 cm³ of water gave, after solvent evaporation on a cold rotavaporator, an oil that slowly crystallised at room temperature (**CAUTION**) to give 46.7 g of **7** (3 wt% H₂O, 15 wt% impurities). Yield of active compound: 38.6 g (83%). Compound **7** was recrystallised from petroleum ether at 0°C. Mp 25–26°C; *t*_{1/2} (10 h) = 71.9°C; HRMS (CI): *m/z* = calcd. for C₃₄H₅₀O₄ (M⁺) 522.37089, found 522.3699; IR: $\bar{\nu}$ = 3050 w, 2927 s, 2857 s, 1787 m, 1763 s, 1691 m, 1610 s, 1466 m, 1417 m, 1228 s, 1178 m, 1028 m, 997 s, 909 m, 851 w, 735 s cm⁻¹; ¹H NMR (CDCl₃): δ = 7.94 (d, *J* = 9 Hz, H-3, H-7), 7.31 (d, *J* = 9 Hz, H-4, H-6), 2.69 (t, *J* = 6 Hz, H-8), 1.65 (m, H-9), 1.27 (m, H-10–H-16), 0.89 (t, *J* = 6 Hz, H-17) ppm; ¹³C NMR (CDCl₃): δ = 163.18 (C-1), 122.94 (C-2), 129.82 (C-3, C-7), 128.88 (C-4, C-6), 150.15 (C-5), 36.13 (C-8), 31.88 (C-9), 31.05 (C-10), 29.57, 29.53, 29.43, 29.30, 29.20 (C-11–C-15), 22.67 (C-16), 14.10 (C-17) ppm.

Note: Known substituted bis(benzoyl) peroxides, namely bis(*p*-toluoyl) peroxide, bis(*m*-toluoyl) peroxide, bis(*o*-toluoyl) peroxide, and bis(*p*-ethylbenzoyl) peroxide [4], have also been prepared in an identical manner.

Bis(3,4-dimethoxybenzoyl) Peroxide (8, C₁₈H₁₈O₈)

A 75.0 g of 30 wt% aqueous H₂O₂ (662 mmol) in 100 cm³ of H₂O solution was added to a 60.0 g of 30 wt% aqueous NaOH (450 mmol) solution at –5°C within 20 min. The temperature was not allowed to rise above 15°C. The mixture was stirred for a further 20 min, then cooled to 5°C. A 13 wt% solution of STAC (10 cm³) was added to the mixture. A solution of 380.0 g of 4-dimethoxybenzoyl chloride (398.7 mmol) in 300 cm³ of butanone was added within 45 min to the cooled, stirred reaction mixture whereby the temperature rose to 15°C. Stirring was continued for another 30 min. Then 15.0 g of NaHCO₃ (178 mmol)

were added to the solution and the reaction mixture was diluted with H₂O to 1 dm³. The fine white suspension was filtered and the product was washed with water to give 28.00 g of wet **8** (38 wt% H₂O). Yield of active material: 17.4 g (24%). Compound **8** was recrystallised from chloroform. (**CAUTION, this peroxide decomposes at room temperature**). $t_{1/2}$ (10 h) < 35°C; IR: $\bar{\nu}$ = 3105 w, 3040 w, 2960 m, 2940 w, 2843 w, 1753 s, 1685 s, 1601 s, 1516 s, 1465 m, 1420 m, 1348 w, 1295 m, 1270 s, 1220 m, 1173 m, 1024 m, 909 s, 734 s cm⁻¹; ¹H NMR (CDCl₃): δ = 7.51 (d, J = 2.0 Hz, H-3), 6.92 (d, J = 8.5 Hz, H-6) 7.72 (dd, J = 8.5, 2.0 Hz, H-7), 3.24 (s, H-8, H-8') ppm; ¹³C NMR (CDCl₃): δ = 162.93 (C-1), 117.51 (C-2), 111.78 (C-3), 148.90 (C-4), 154.00 (C-5), 110.54 (C-6), 124.08 (C-7), 56.00 (C-8, C-8') ppm.

Bis(p-n-propoxybenzoyl) Peroxide (10, C₂₀H₂₂O₆)

A 40.0 g of 30 wt% aqueous H₂O₂ (352 mmol) in 60 cm³ of H₂O solution was added to a 37.0 g of 30 wt% aqueous NaOH (278 mmol) solution at -5°C within 10 min and then stirred for a further 20 min. A 13 wt% solution of STAC (7 cm³) was added to the sodium peroxide at 5°C. A solution of 50.0 g of *p-n*-propoxybenzoyl chloride (252 mmol) in 20 cm³ of butanone was added within 30 min to the cooled, stirred reaction mixture whereby the temperature rose to 15°C. The reaction mixture became a white suspension and was then treated with 30 cm³ of butanone to further enhance stirring at room temperature. H₂O (800 cm³) was added to facilitate complete precipitation, the mixture was filtered, and the product was washed with H₂O to give 62.6 g of wet **10** (26 wt% H₂O, 28% impurity due to 4-*n*-propoxybenzoic acid). Yield of active compound: 32.6 g (72%). Compound **10** was purified by recrystallisation from petroleum ether:chloroform (1:1). $t_{1/2}$ (10 h) = 38°C; HRMS (CI): m/z = calcd. for C₂₀H₂₂O₆ (M⁺) 358.14164, found 358.1415; IR: $\bar{\nu}$ = 2970 m, 2960 m, 2870 w, 1783 m, 1753 s, 1670 s, 1508 s, 1473 m, 1426 m, 1317 m, 1252 s, 1167 m, 1065 m, 970 m cm⁻¹; ¹H NMR (CDCl₃): δ = 8.06 (d, J = 9 Hz, H-3, H-7), 6.94 (d, J = 9 Hz, H-4, H-6), 4.00 (t, J = 7 Hz, H-8), 1.85 (hex, J = 7 Hz, H-9), 1.056 (t, J = 7 Hz, H-10) ppm; ¹³C NMR (CDCl₃): δ = 163.67 (C-1), 117.98 (C-2), 132.34 (C-3, C-7), 114.18 (C-4, C-6), 162.8 (C-5), 69.74 (C-8), 22.44 (C-9), 10.46 (C-10) ppm.

Determination of $t_{1/2}$ (10 h) of Substituted Bis(benzoyl) peroxides

To relatively compare the individual half life of bis(benzoyl)peroxides, it is typical to quote the temperature (in °C) at which half of the compound has decomposed after 10 h ($t_{1/2}$ (10 h)). The method that we used for determining the temperature of $t_{1/2}$ (10 h) involved the analyses of the amount of peroxide in a 0.5 to 1 mM methanolic solution remaining after exactly 10 h at different temperatures. A plot of concentration versus temperature (10 h) gave the precise temperature at which half of the peroxide had decomposed. The methanolic solution (10 μ l) was injected and analysed by reverse phase HPLC. A 250 \times 10 mm ALLTIMA C18 column was used and the suitable mobile phase was 80% MeOH – 20% H₂O. The UV-detector was set at λ = 254 and 280 nm to detect the peroxide. The main decomposition products encountered were the substituted benzoic acid and the corresponding methyl ester, both compounds had retention times quite different from the peroxide.

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