Decomposition of Peroxydecanoic Acid using BCHPC [Di(4-*tert*-butylcyclohexyl) Peroxydicarbonate] under Argon Atmosphere

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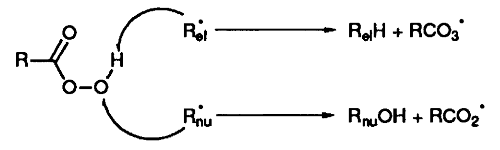
Using BCHPC as a source of alkoxycarbonyloxyl radical at moderate temperature in benzene or cyclohexane and in the absence of O_2 (under argon), the peroxydecanoic acid RCO_3H is transformed into nonan-1-ol ROH in good yield. A mechanism, implying the acylperoxyl radical $RCO_3^\bullet$ as an intermediate, is proposed.

It is well established that the thermal decomposition mechanism of a peroxyacid can proceed through radical mechanisms.[1] The initiating step (Scheme 1) is the thermal rupture of the weak peroxidic O–O bond of the peroxyacid [reaction (1)]. When R is aliphatic, the decarboxylation rate of the acyloxy radical[2] is *ca.* 10^{10} s^{-1} [reaction (2)]. The peracid contains two radicophile centres (Scheme 2). With nucleophilic radicals $R_{nu}^\bullet$ (alkyl radicals mainly), the site of attack is the peroxidic oxygen of the O–O bond leading to alcohol $R_{nu}OH$. With electrophilic radicals $R_{el}^\bullet$ (oxygenated radicals mainly), there is no reaction upon the peroxyacid O–O bond and abstraction of the peroxidic H leading to the acylperoxy radical $RCO_3^\bullet$ has been postulated.

$$RCO_3H \longrightarrow RCO_2^\bullet + {}^\bullet OH \qquad (1)$$

$$RCO_2^\bullet \xrightarrow{\text{Fast}} R^\bullet + CO_2 \qquad (2)$$

Scheme 1 Initiation



Scheme 2 Peroxyacid reactivity towards electrophilic and nucleophilic radicals

In these free-radical mechanisms, the key factor is the presence or absence of oxygen. At reflux temperature (Scheme 3), the oxygen is eliminated to a great extent from the medium (the more vigorous the reflux, the less the quantity of dissolved oxygen in the medium). The nucleophilic radical $R^\bullet$ abstracts the H from the solvent (in the case of an H-donor solvent ΣH) leading to RH and the radical $\Sigma^\bullet$ [reaction (3)] or reacts with the peroxyacid O–O bond leading to ROH, CO_2 and the radical $R^\bullet$ [reaction (4a)]. The nucleophilic $\Sigma^\bullet$ can also react with the peroxyacid leading to ΣOH, CO_2 and the radical $R^\bullet$ [reaction (4b)]. Below the reflux temperature (Scheme 4), the nucleophilic radicals $R_{nu}^\bullet$ ($R^\bullet$ or $\Sigma^\bullet$) are quickly trapped by dissolved oxygen [reaction (5)]. The electrophilic radical $R_{nu}O^\bullet$ abstracts the H from the peroxyacid or solvent leading to $R_{nu}OH$ and, respectively, to the acylperoxy radical $RCO_3^\bullet$ [reaction (7)], or nucleophilic radical $\Sigma^\bullet$ [reaction (8)]. Our purpose was to study the peroxyacid decomposition mechanism in the presence of different types of peroxide source of oxygenated radicals in order to favour reaction (7). We chose BCHPC† [di(4-*tert*-butylcyclohexyl) peroxydicarbonate] which is used to induce the polymerization of alkenes. BCHPC seemed appropriate because it decomposes, at low temperature, into free electrophilic radicals which could induce the peroxyacid decomposition by H-abstraction and lead to the acylperoxy radical $RCO_3^\bullet$ according to reaction (7).

$$R^\bullet + \Sigma H \longrightarrow RH + \Sigma^\bullet \qquad (3)$$

$$R^\bullet + RCO_3H \longrightarrow ROH + R^\bullet + CO_2 \qquad (4a)$$

$$\Sigma^\bullet + RCO_3H \longrightarrow \Sigma OH + R^\bullet + CO_2 \qquad (4b)$$

Scheme 3 Formation of alcohol

$$R_{nu}^\bullet + O_2 \longrightarrow R_{nu}OO^\bullet \qquad (5)$$

$$2R_{nu}OO^\bullet \longrightarrow 2R_{nu}O^\bullet + O_2 \qquad (6)$$

$$R_{nu}O^\bullet + RCO_3H \longrightarrow R_{nu}OH + RCO_3^\bullet \qquad (7)$$

$$R_{nu}O^\bullet + \Sigma H \longrightarrow R_{nu}OH + \Sigma^\bullet \qquad (8)$$

$$R_{nu} = R \text{ or } \Sigma$$

Scheme 4

Results

The decomposition mechanism for dicyclohexyl peroxydicarbonate was described by Van Sickle[3] in 1970 and we obtained analogous results with BCHPC. The radical mechanism of BCHPC decomposition is an induced one (Scheme 5); the first step is the formation of radicals by thermal rupture of the weak peroxidic O–O bond [reaction (9)]. The radical $InO^\bullet$, which has a slow decarboxylation rate ($k \le 10^5$ s^{-1})[4] compared to an acyloxy radical $RCO_2^\bullet$ (k *ca.* 10^{10} s^{-1}),[2] abstracts the α-hydrogen of the cyclohexane ring of BCHPC [reaction (10)]. The carbonic acid is not stable and decarboxylates to give *tert*-butylcyclohexanol [reaction (11)]. The radical $InC^\bullet$ undergoes a double β-fragmentation leading to the radical $InO^\bullet$ and *tert*-butylcyclohexanone [reaction (12)]. According to the present mechanism, the ratio between *tert*-butylcyclohexanol and *tert*-butylcyclohexanone formed should be 1 : 1.

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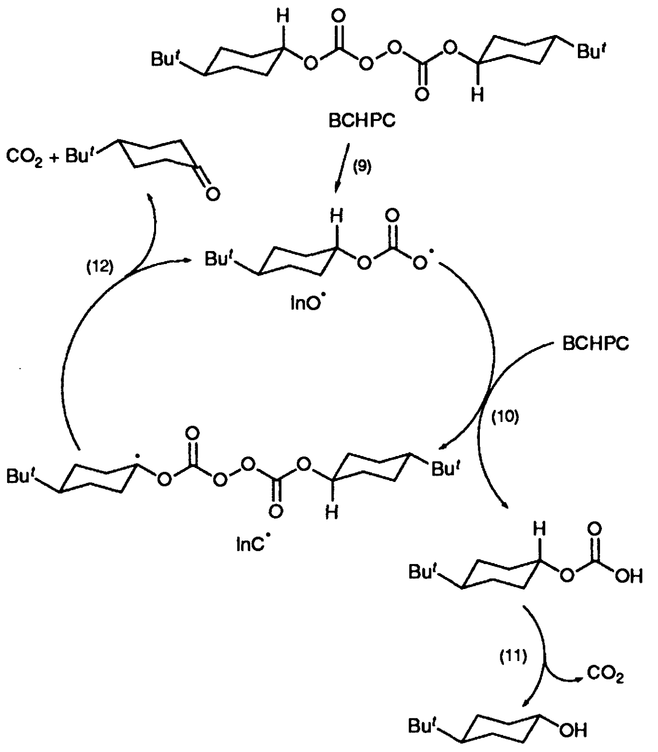
† BCHPC was furnished by Interox Chemicals (U.K.).

Table 1 Decomposition of peroxydecanoic acid (0.1 mol dm^{-3}) in cyclohexane

Run	T/°C[a]	Gaseous atmosphere	Product composition[c]						Total yield[d]	SOH[e]	$t_{\frac{1}{2}}$/min	k_{exp}/10^{-3} s^{-1}[f]
			RCO_2H	$R_{-1}CO_2H$	ROH	$R_{is}OH$[g]	RH	R(−H)				
1	78	Air	90	3	1	—	1	3	98	26	840	0.1
2	78	Argon[b]	28	8	53	4	10	1	104	17	35	3.3
3	90	Air	12	2	63	8	18	1	104	20	15	7.7
4	90	Argon[b]	13	3	69	2	17	1	105	19	7	17.0

[a] External oil bath. [b] Gaseous flow through the solution. [c] In moles per 100 moles of peroxydecanoic acid; R = nC_9H_{19}; R_{-1} = nC_8H_{17}. [d] In % of recovered nonyl substituent R in the decomposition products. [e] Solvent product: cyclohexanol. [f] k_{exp}/s^{-1} is first order. [g] R_{is} = $CH_3(CH_2)_4CH^{\cdot}(CH_2)_2CH_3$ and/or $[CH_3(CH_2)_3]_2CH^{\cdot}$.[1,5]



Scheme 5 BCHPC decomposition mechanism

Thermal Decomposition of Peroxydecanoic Acid in Cyclohexane under Various Gaseous Atmospheres.—Decomposition reactions of peroxydecanoic acid have been carried out under different conditions (see Table 1). In order to evaluate the effect of dissolved oxygen on the thermal decomposition products, argon has been used as the gaseous atmosphere. Below reflux temperature the thermal decomposition of perdecanoic acid in cyclohexane depends on the gaseous atmosphere. Under air, it leads, as previously described with peroxydodecanoic acid,[6] quantitatively to decanoic acid (run 1). Under argon, the major product is nonan-1-ol ROH (run 2). Furthermore, the half-life of peroxydecanoic acid in run 1 is *ca.* 24 times greater than in run 2. The sole difference between these two experiments was the gaseous atmosphere; in the presence of argon, the quantity of dissolved oxygen in the medium is considerably reduced, and consequently, there is formation of alcohol ROH according to Scheme 3. At reflux temperature, the influence of argon on the decomposition products is less important; in fact, we observe about the same results with and without argon. This is easily understandable because, at reflux, the oxygen was almost totally eliminated and the contribution of argon is negligible. However, the presence of a flux of argon through the medium seems to increase the overall rate of decomposition. The presence or absence of argon does not seem to influence the quantity of cyclohexanol coming from cyclohexane hydroxylation. It is clear that the argon plays an important role and contributes to the elimination of the oxygen from the medium when we are working below reflux temperature. The use of a gaseous flow of argon through the medium appears to be a good alternative to reflux as a means of eliminating O_2 at low temperature.

Decomposition of Mixtures of BCHPC and Peroxydecanoic Acid in Benzene and Cyclohexane under Argon.—The aim was to bring about low temperature peroxydecanoic acid decomposition initiated by BCHPC. In benzene, at 55 °C and under argon, the peroxydecanoic acid alone does not decompose; the results in Table 2 indicate clearly that the BCHPC induces the peroxydecanoic acid decomposition. A very striking result is the presence of the alcohol ROH in a good yield. In contrast to the present results the thermal decomposition of peroxydecanoic acid, in benzene[1] at reflux temperature, leads mainly to the corresponding acid (40%). Hence, it may be assumed that these two mechanisms are different. It should be noted that the product distribution is insensitive to the initial peracid concentration. Nevertheless the half-life time of the peracid is shorter as the initial concentration in peracid decreases.

In cyclohexane (*cf.* Table 3), as in benzene, the major product is the ROH alcohol. Furthermore, the following differences with the preceding experiments given in Tables 1 and 2 must be quoted. The quantity of decanoic acid RCO_2H is negligible; *i.e.* the decarboxylation is nearly quantitative. Small quantities of RCO_2R and R-R are detected. This was not the case for the thermal decomposition of the peroxydecanoic acid alone, even at 90 °C under argon (Table 1) or, in benzene, in the presence of BCHPC (Table 2). There is no significant difference in the product ratio when the BCHPC concentration increases from 0.05 to 0.2 mol dm^{-3} except the quantity of cyclohexanol which rises with increasing initial BCHPC concentration. The higher the initial concentration of BCHPC, the faster the decomposition rate of peroxydecanoic acid. The reaction is slightly slower in benzene than in cyclohexane (compare run 1 in Table 2 to run 2 in Table 3).

Discussion

Reaction in Cyclohexane.—The first step is the thermal rupture of the peroxidic O–O bond of BCHPC [reaction (9) in Scheme 5] leading to the electrophilic radical IO$^\cdot$. Then IO$^\cdot$ can abstract either H from the peroxyacid leading to the electrophilic acylperoxyl radical [reaction (13)], or H from

$$IO^\cdot + nC_9H_{19}CO_3H \longrightarrow IOH + nC_9H_{19}CO_3^\cdot \quad (13)$$

cyclohexane leading to the nucleophilic cyclohexyl radical [reaction (14)]. Reaction (14) is favoured over reaction (13).

$$IO^\cdot + C_6H_{12} \longrightarrow IOH + C_6H_{11}^\cdot \quad (14)$$

Table 2 Decomposition of mixtures of BCHPC (0.1 mol dm^{-3}) and peroxydecanoic acid in benzene under an argon atmosphere[a] at 55 °C

Run	$[RCO_3H]_0$[b]/ mol dm^{-3}	Product composition[c] RCO_2H	$R_{-1}CO_2H$[h]	ROH	RH	Total yield[d]	$t_{1/2}$[f]
1	0.1	13	5	65	7	90	20
2	0.05	14	3	66	8	91	<10
3	0.01	10	0	70	nm[e]	80	nd[g]

[a] Under positive gaseous pressure. [b] Initial concentration of peroxydecanoic acid. [c] In moles per 100 moles of peroxydecanoic acid. [d] In % of recovered nonyl substituent R in the decomposition products. [e] Non-measured products. [f] Half-life time in min. [g] Not determined. [h] $R_{-1} = nC_8H_{17}$.

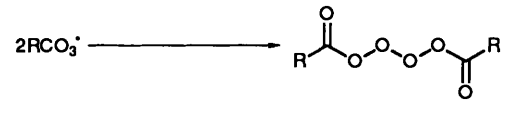
Table 3 Decomposition of mixtures of BCHPC and peroxydecanoic acid (0.1 mol dm^{-3}) at 55 °C in cyclohexane under an argon atmosphere at 55 °C

Run	$[BCHPC]_0$[a]/ mol dm^{-3}	Product composition[b] RCO_2H	ROH	RH	R(−H)	RR	RCO_2R	Total yield[c]	ΣOH[d]	$t_{1/2}$[e]
1	0.050	~0	59	19	1	1	3	89	30	35
2	0.100	~0	58	19	2	3	5	97	30	15
3	0.150	~0	53	20	1	2	3	85	33	5
4	0.175	~0	53	21	2	5	7	101	37	4
5	0.200	~0	53	23	8	3	5	101	45	3

[a] Initial concentration of BCHPC. [b] In moles per 100 moles of peroxydecanoic acid. [c] In % of recovered nonyl substituent R in the decomposition products. [d] Solvent product: cyclohexanol. [e] Half-life time in min.

Indeed, the bond energies C–H in cyclohexane and O–H in peroxyacid[7,8] are about the same (94 kcal mol^{-1}). However, since cyclohexane is the solvent, the probability for the radical IO$^•$ to react with it is much greater than to take part in reaction (13). Furthermore, the radical polar effect favours reaction (14) over reaction (13).

Hence, the decomposition of the peroxyacid is induced, to a great extent, by the reaction of cyclohexyl radicals with the peroxyacid leading to ΣOH, CO_2, ROH and alkyl radicals R$^•$ *via* Scheme 3. Nevertheless, this does not explain the formation of the ester RCO_2R and the dimer RR. Considering the concentration effect, the H-abstraction from cyclohexane [reaction (14)] is favoured in comparison with H-abstraction from the peroxyacid [reaction (13)]; however, this latter reaction can occur, even in small proportions, and because of the low reactivity of the acylperoxy radicals $RCO_3^•$, their recombination leading to the tetroxide could be possible [reaction (15)].[9,10] The decomposition of the tetroxide can follow two different processes: the first one postulated by McDowell and Sifniades[9] involves a cyclic process leading to the corresponding diacyl peroxide [reaction (16)]. The second process[10] involves a cage collapse including different intervening cages leading to disproportionation and/or dismutation products [RCO_2R, RR, RH and R(−H)] in low yield (Scheme 6). On the other hand, radicals R$^•$ and $RCO_2^•$ (which fragments rapidly to CO_2 and R$^•$) escape from the cage. Then the radical R$^•$ induces the decomposition of the peroxyacid leading to ΣOH, CO_2, ROH *via* Scheme 3. However, we are unable to distinguish between these two processes because they can lead to the same products. The diacyl peroxide* has, under our conditions, about the same decomposition rate as the BCHPC. Furthermore, it has been reported[11] that the decomposition of dodecanoyl peroxide in hydrocarbon at 80 °C leads (in mole per mole of peroxide) to dodecanoic acid (0.08), undecyl dodecanoate (0.31), n-docosane (0.32), n-undecane (0.67) and n-undec-1-ene (0.07). Hence, we can suggest that the tetroxide can lead to the cage 2 through reactions (17) and (18) and/or reactions (16) and (19). The fact that the ratio RH/R(-H) is, in cyclohexane, on average equal to 15 and that the quantities of RCO_2R and RR are about constant indicates that the initial concentration of BCHPC does not affect the ratio of products coming from the cage reactions.



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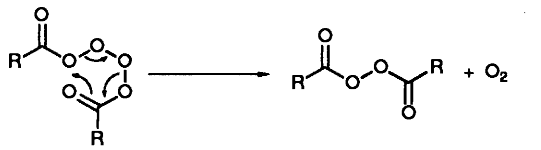

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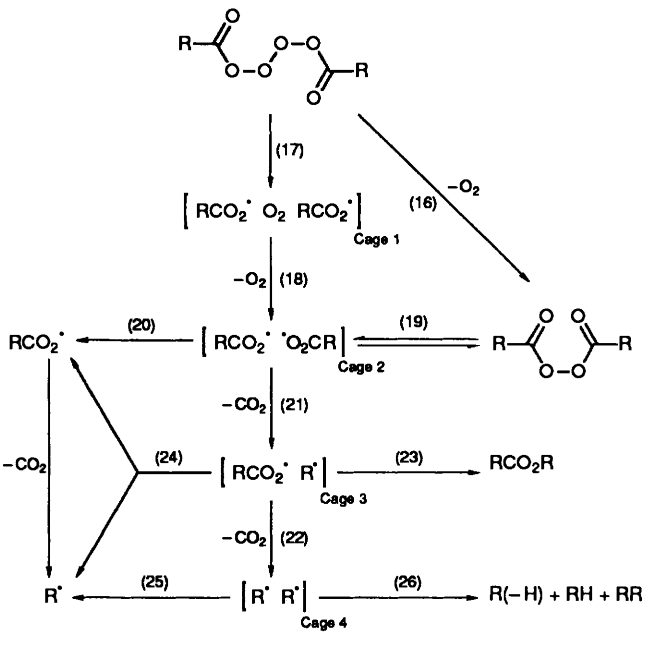

Scheme 6

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* Organic peroxides and other initiators; Review from Interox Company.

Reaction in Benzene.—In benzene, there is no H-abstraction reaction from the solvent. The sole reaction which can occur is the H-abstraction from the peroxyacid leading to the acylperoxyl radical $RCO_3^\bullet$ [reaction (13)]. In benzene, we do not observe RR, R(−H) and RCO_2R (Table 2) in contrast with the decompositions in cyclohexane (Table 3). One reason for this main difference in the results obtained in benzene and cyclohexane could be that in benzene $RCO_3^\bullet$ should be stabilized by solvation with the aromatic ring. This will prevent dimerization [reaction (15)], so the tetroxide and the subsequent products (Scheme 6) will not be formed. It has been reported[12,13] for the electrophilic *tert*-butoxyl radical that solvation by polar or polarizable solvents favours the β-fragmentation. For the acylperoxyl radical, this solvent effect should favour analogous β-fragmentation into R–C$^\bullet$=O and O_2 [reaction (28) in Scheme 7]. R–C$^\bullet$=O, a nucleophilic radical,[14]

$$RCO_3^\bullet + PhH \rightleftharpoons RCO_3^\bullet \cdots PhH \qquad (27)$$

$$RCO_3^\bullet \longrightarrow R\dot{C}O + O_2 \qquad (28)$$

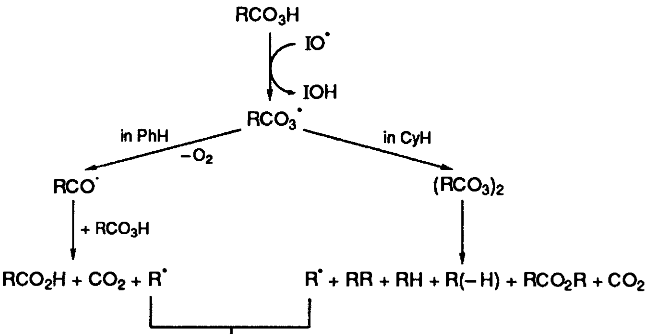
$$R\dot{C}O + RCO_3H \longrightarrow RCO_2H + R^\bullet + CO_2 \qquad (29)$$

Scheme 7

reacts upon the peroxidic oxygen leading to the acid RCO_2H, CO_2 and $R^\bullet$ [reaction (29)]. This reaction is exothermic by *ca.* 45 kcal mol^{-1}.[15] Finally, the alkyl radical $R^\bullet$ initiates the decompositon in alcohol *via* Scheme 3. The fact that the ratio RH/R(−H) is, in cyclohexane, on average equal to 15, and that the quantities of RCO_2R and RR are about constant, indicates that the initial concentration of BCHPC does not affect the ratio of products coming from the cage reactions.

Conclusions

In comparison with the thermal decomposition of the peroxyacid, the use of BCHPC permits us to induce the decomposition of the peroxyacid at low temperatures with a short reaction time leading principally to the alcohol ROH (~70%). Both mechanisms, in cyclohexane or in benzene, are summarized in Scheme 8. In cyclohexane, the absence of acid RCO_2H and the presence of RR, RH, R(−H) and RCO_2R indicates that the acyl radical $RCO^\bullet$ is not formed and the reaction is going partly through the dimer $(RCO_3)_2$. In benzene the absence of RR, RH, R(−H) and RCO_2R and the presence of RCO_2H, show that radicals $RCO_3^\bullet$ do not dimerize but, by β-fragmentation, lose O_2 and lead to $RCO^\bullet$. During the decomposition of peracids in cyclohexane without BCHPC, there is no formation of the acylperoxyl radical $RCO_3^\bullet$ and, consequently, of $RCO^\bullet$ since the products resulting from the $(RCO_3)_2$ dimer are not observed (Table 1). This implies that the mechanism proposed[1] for the formation of acid, going through acylperoxyl and acyl radicals, is not valid, and that the transformation of peracid into acid in these conditions takes place through an unknown mechanism. We can conclude that the use of BCHPC leads, by induced decomposition, to a good yield of the primary alcohol ROH from the corresponding aliphatic peroxyacid RCO_3H.



Scheme 8

Experimental

Peroxydecanoic acid alone and its mixtures with BCHPC were decomposed in cyclohexane and benzene at different concentrations under various gaseous atmospheres. The rates of disappearance of peroxyacid and BCHPC were followed by iodometry[16] and/or FT-IR, monitoring the characteristic frequencies[17] of the carbonyl and hydroxyl groups of peroxyacid and BCHPC. The reactions were stopped when the peroxyacid had completely disappeared. The reaction products were qualitatively and quantitatively analysed by GC.

Peroxydecanoic Acid Preparation.—Decanoic acid (8.62 g, 50 mmol) was dissolved in concentrated sulfuric acid (25 cm^3) at 25 °C with mechanical stirring. The mixture was cooled to 0 °C to give a homogeneous paste. 30% H_2O_2 (10.5 cm^3, 100 mmol) was added dropwise for 35–40 min slowly enough to keep the temperature at *ca.* 5 °C. After the addition was completed, the mixture was kept at *ca.* 5 °C while stirring for 90 min. The suspension was then poured into crushed ice (200 g) and the white peroxyacid crystals were filtered, washed with saturated $(NH_4)_2SO_4$ solution (4 × 25 cm^3), then distilled water, and dried under vacuum for one day. White crystals (9.30 g, 98% yield) with a purity of 88% or more were obtained. Crystallization from pentane afforded pure peroxydecanoic acid (purity > 99%). The purity was determined by iodometry and FT-IR.

Typical Peroxyacid and BCHPC Mixture Decomposition Procedure.—In a three-necked round-bottom flask (50 cm^3), fitted with gas inlet and a condenser, was placed a solution (20 cm^3) of BCHPC and peroxydecanoic acid in benzene or cyclohexane which had been previously saturated with argon during 30 min. A small positive pressure was then applied above the solution and the flask was then immersed in the oil bath. The external oil bath temperature was kept at 55 °C ± 1 °C. The reaction was followed by iodometry and FT-IR. IR absorptions; ν_{max}/cm^{-1} peroxyacid 3270 (OH) and 1747 (C=O), acid 1719 (C=O) and BCHPC 1796 (C=O).

At the end of the reaction (when more than 95% of the starting peroxyacid had decomposed), the solution was cooled on a water–ice bath and the product distributions were analysed by GC on an apolar column DB5 (30 m) using three internal standards.

Acknowledgements

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