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ORIGINAL PAPER

Synthesis and thermal properties of asymmetrical azo-peresters

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Abstract New asymmetrical azo-perester derivatives of *tert*-butyl and *tert*-amyl hydroperoxides were obtained by reacting azo acids with hydroperoxides in the presence of *N*,*N*′-carbonyldiimidazole. The obtained azo-peresters possess two labile functional groups: the azo group and the perester group. Data from dynamic differential scanning calorimetry (DSC) experiments indicate that the azo groups decompose at somewhat lower temperatures than the perester groups.

Keywords Differential scanning calorimetry · Bifunctional initiators · NMR spectroscopy · Peroxides · Diazo compounds

Introduction

Polymeric materials are extensively employed in nearly all branches of industry. Polymers with unique physical and chemical properties have particular importance. Unfortunately, most homopolymers contain a limited range of molecular functionality and consequently possess a limited set of macroscopic properties. Therefore, it is often necessary to obtain required features through specially designed tailor-made copolymers with more diverse structures. Those copolymers can be obtained with different polymerisation techniques, and can be modified with different additives. To prepare such copolymers, bi- and polyfunctional initiators are frequently used. These initiators contain at least two reactive groups in their structure and can initialise polymerisation processes according to specific mechanisms (ionic, free radical etc.). Azo-peroxy compounds constitute one important class of such bifunctional initiators. These molecules contain labile azo and peroxy groups that possess different thermal and/or photochemical stabilities. Consequently, these compounds undergo discrete thermal decomposition processes at two different temperatures. This allows them to initialise free radical processes in a one-pot, two-stage fashion.

Most research about azo-peroxy compounds has focused on their role in polymerisation processes, but there is surprisingly little data regarding their thermal stability. This work expands upon our previous research concerning symmetrical azo-peresters [1].

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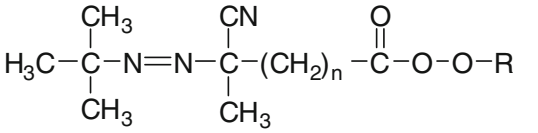
Results and discussion

In this work, we report the preparation and characterisation of new asymmetrical compounds, as described in Scheme 1.

Asymmetrical azo-peresters **3** and **4** were obtained by reacting appropriate azo-functionalised carboxylic acids **2** with *tert*-alkyl hydroperoxides in the presence of *N*,*N*′-carbonyldiimidazole.

Asymmetrical carboxylic acids containing azo groups were first obtained according to the procedure described by Shaikh [2] from suitable ketoacids **1**, sodium cyanide, and *tert*-butylhydrazine hydrochloride. Among this set of products, only 4-(*tert*-butylazo)-4-cyanopentanoic acid **2a** has been previously described (in a patent) [3], and in this



a n = 2 **3** R = -C(CH$_3$)$_3$
b n = 3 **4** R = -C(CH$_3$)$_2$CH$_2$CH$_3$
c n = 4

Scheme 1

case, relatively little information about this compound was reported (Scheme 2).

Asymmetrical carboxylic acids **2** that contain azo groups were obtained in high purities and with satisfactory yields. Acids like 4-(*tert*-butylazo)-4-cyanopentanoic acid (**2a**), 5-(*tert*-butylazo)-5-cyanohexanoic acid (**2b**), and 6-(*tert*-butylazo)-6-cyanoheptanoic acid (**2c**) were used to obtain a series of asymmetrical azo-peresters with *tert*-amyl and *tert*-butyl substituents. To obtain these compounds, we employed a method described by Staab [4] that was previously used to obtain esters, peresters, and azo-peresters directly from carboxylic acids [5, 6]. Staab's method was modified by:

- Usage of a greater excess of hydroxide to carboxylic acid, which increased yields
- Increasing the reaction time, to compensate for a higher reaction mixture viscosity
- Usage of a more concentrated NaOH solution for washing the crude product mixture, in order to better remove excess hydroperoxide.

This method generates an acylating agent in situ by reacting *N*,*N*′-carbonyldiimidazole with a carboxylic acid containing an azo group (Scheme 3). There is no need to separate and purify the acylating agent, because it reacts immediately with the hydroperoxide reagent. The reaction is carried out using tetrahydrofuran (THF) as the solvent. This prevents the decomposition of the azo-perester products, as was observed during preliminary studies in chlorinated solvents. In spite of using a carboxylic acid reagent, the reaction mixture has a slightly basic pH, which protects the peroxy product from decomposition. Unfortunately, this method is limited due to the sensitivity of *N*,*N*′-carbonyldiimidazole and the intermediate acylating agent to traces of water, which causes their decomposition.

The asymmetrical azo-peresters **3** and **4** were prepared in moderate yields. There was no obvious correlation between substituent or carbon chain length and yield. The structure of each compound was confirmed by elemental analysis and spectroscopic analysis by ^{1}H NMR, ^{13}C NMR, and IR.

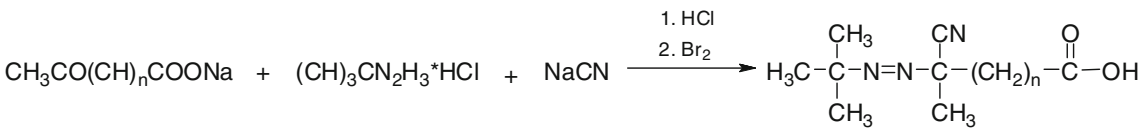
Thermal decomposition of asymmetrical azo-peresters

The thermal decomposition of the obtained asymmetrical azo-peresters **3** and **4** was evaluated by differential scanning calorimetry (DSC). Results for two selected examples are shown below—namely, for *tert*-butyl (Fig. 1) and *tert*-amyl hydroperoxide derivatives (Fig. 2) of 4-(*tert*-butylazo)-4-cyanopentanoic acid (**2a**).

In these figures, there are two peaks indicating the exothermic decomposition of the azo and perester groups. In all cases, the first peak (at lower temperature) corresponds to the decomposition of the azo group, and the second peak (at higher temperature) corresponds to the decomposition of the perester group. Because some of the azo-perester products were obtained in the form of an oil, peaks corresponding to an endothermic melting process were observed for a limited subset of products.

To confirm the sequence of decomposition in asymmetrical azo-peresters, an analogical test was conducted using symmetrical compounds [1]. The experiments consisted of heating two selected azo-peresters (**3a** and **4c**) with and without 1% cobalt stearate. The results are given in Table 1.

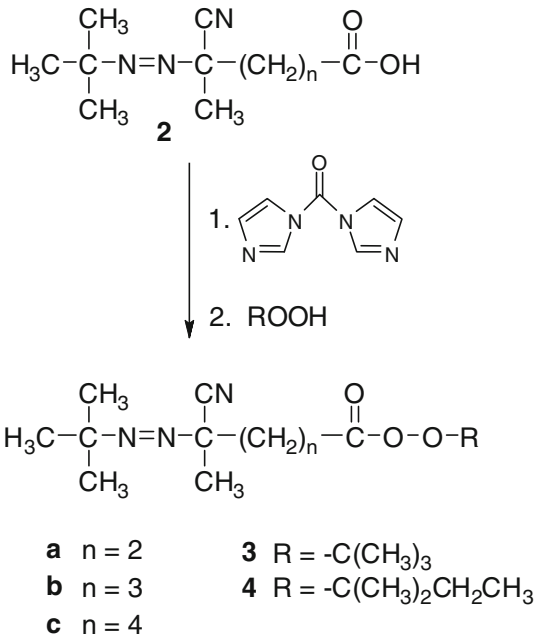
The obtained results show that the addition of a cobalt salt has no influence on the temperature of azo group decomposition (T_p) and changes the corresponding peak shape only slightly. However, the same salt appears to have a greater influence on perester group decomposition. T_p values for the peaks corresponding to perester group decomposition shift to lower temperatures, which in the case of **3a** causes the peak from the perester group



1 **2**

a n = 2
b n = 3
c n = 4

Scheme 2



Scheme 3

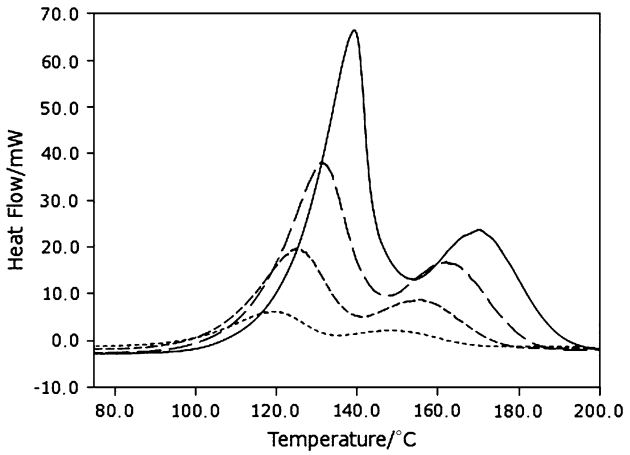


Fig. 1 DSC curves for samples of *tert*-butyl 4-(*tert*-butylazo)-4-cyanoperoxypentanoate (**3a**) at different heating rates: *solid line* 20 °C/min, *large-dashed line* 10 °C/min, *medium-dashed line* 5 °C/min, *small-dashed line* 2.5 °C/min

decomposition to overlap with the peak from the azo group decomposition. In the case of **4c**, a similar effect can be observed, but the coverage is not total.

Data regarding the T_p values for both labile groups in the asymmetrical azo-peresters are shown in Tables 2 and 3 for *tert*-butyl and *tert*-amyl hydroperoxide derivatives, respectively.

The experimental data gathered in Tables 2 and 3 show that in asymmetrical derivatives of *tert*-amyl hydroperoxide, perester groups decompose at lower temperatures than in analogues that bear a *tert*-butyl group. A similar situation was observed for symmetrical derivatives [1].

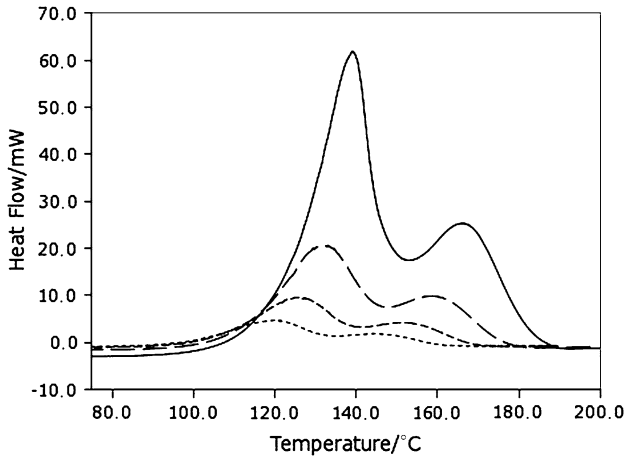


Fig. 2 DSC curves for samples of 1,1-dimethylpropyl 4-(*tert*-butylazo)-4-cyanoperoxypentanoate (**4a**) at different heating rates: *solid line* 20 °C/min, *large-dashed line* 10 °C/min, *medium-dashed line* 5 °C/min, *small-dashed line* 2.5 °C/min

Table 1 Maximum exothermic temperatures (T_p) of asymmetrical azo-peresters decomposed in the presence of 1% by mass of cobalt stearate (constant heating rate 10 °C/min)

Compound	Temperature (°C)			
	With addition of salt		Without addition of salt	
	–N=N–	–O–O–	–N=N–	–O–O–
3a	129.7	–[a]	131.0	162.2
4c	135.9	136.6[b]	137.3	155.8

[a] Peak invisible on DSC (whole peak of perester group decomposition is buried by the azo group decomposition peak)

[b] Peak seen on DSC under main peak

Table 2 Maximum exothermic temperatures (T_p) of asymmetrical azo-peresters with *tert*-butyl substituents under various heating rates

β (°C/min)	Temperature (°C)					
	3a		**3b**		**3c**[a]	
	–N=N–	–O–O–	–N=N–	–O–O–	–N=N–	–O–O–
1	112.5	140.1	112.9	135.5	112.6	136.2
2.5	119.0	148.4	122.5	144.9	123.5	144.3
5	125.3	155.4	128.2	151.9	128.9	151.0
10	131.0	162.2	133.6	158.5	135.4	158.6
20	139.3	169.8	142.1	166.6	142.9	166.7

[a] Compound obtained as an oil

Additionally, the maximum exothermic temperatures corresponding to azo group decomposition within asymmetrical compounds show analogous behaviour to symmetrical derivatives. The T_p values for azo group decomposition within derivatives bearing a *tert*-amyl group are slightly higher than those bearing a *tert*-butyl group.

Table 3 Maximum exothermic temperatures (T_p) of asymmetrical azo-peresters with *tert*-amyl substituents under various heating rates

β (°C/min)	Temperature (°C)					
	4a[a]		**4b**[a]		**4c**	
	–N=N–	–O–O–	–N=N–	–O–O–	–N=N–	–O–O–
1	111.7	136.7	114.7	134.6	115.8	134.2
2.5	120.3	144.5	122.2	142.8	124.0	142.5
5	126.3	151.4	129.1	149.4	130.7	149.1
10	131.9	158.8	135.3	156.1	137.3	155.8
20	139.0	166.5	142.2	163.2	144.1	162.3

[a] Compounds obtained as an oil

Experimental

tert-Butyl hydroperoxide (Merck) was extracted with hexane prior to use. *tert*-Amyl hydroperoxide (Pergan), sodium cyanide (Fluka), *tert*-butylhydrazine hydrochloride, *N*,*N*′-carbonyldiimidazole (Alfa Aesar GmbH & Co KG), and 4-oxopentanoic acid (**1a**, Fluka) were sourced from the indicated vendors and used without additional purification. Diethyl ether was dried over metallic Na (P.P.H. POCH S.A. Gliwice) prior to use. THF (P.P.H. POCH S.A. Gliwice) was dried over metallic Na in the presence of benzophenone and freshly distilled (65–66 °C) prior to use. 5-Oxohexanoic acid (**1b**) was synthesised as described by Bates [7] and 6-oxoheptanoic acid (**1c**) was synthesised as described by Schaeffer [8].

^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Varian Unity Inova-300 spectrometer using TMS as an internal standard. IR spectra were recorded on a Zeiss Specord M 80 spectrometer. The results of elemental analyses agreed favourably with the calculated values. The thermal characteristics of the investigated materials were obtained using a DSC 2010 TA instrument at heating rates of 1, 2.5, 5, 10, or 20 °C/min within a temperature range of −80 to +200 °C. The temperature was calibrated with indium and gallium standards over the whole explored temperature range.

The obtained asymmetrical azo-peresters were kept frozen in glass, tightly closed containers. Azo-peresters can easily decompose at high temperature (over 80 °C) or in the presence traces of amines, transition metal salts, or acidic substances. Because of a lack of literature data about handling such compounds, extreme caution should be undertaken, similar to work with explosive compounds.

General procedure for preparation of asymmetrical carboxylic acids with azo functionality

To a solution of *tert*-butylhydrazine hydrochloride (0.16 mol) in 65 cm^3 water, a solution of sodium cyanide (0.16 mol) in 20 cm^3 water was added slowly under very intensive stirring. The mixture was stirred for an additional 20 min. A solution of 4-oxopentanoic (**1a**), 5-oxohexanoic (**1b**), or 6-oxoheptanoic acid (**1c**) neutralised with sodium carbonate in 25 cm^3 water (0.16 mol of acid) was then slowly added. The final pH of the reaction mixture was around 7. The mixture was subsequently allowed to stir for 8 h and then left for a further 36 h. Then, the reaction mixture was cooled to 5 °C and acidified with concentrated HCl. The acidified reaction mixture was intensively stirred for 30 min. Bromine was then added dropwise until the colour of the mixture indicated the presence of excess reagent. The resulting suspension was stirred for 1 h, and then the reaction mixture was poured onto ice (30 g) and stirred until the ice melted. The reaction mixture was transferred to a freezer to crystallise the product. The obtained precipitate was filtered and recrystallised from CH_2Cl_2.

General procedure for preparation of asymmetrical azo-peresters

A three-necked flask was equipped with a mechanical stirrer, nitrogen supply, and dropping funnel, and a solution of each carboxylic acid with an azo functional group **2** (7.13 mmol) was introduced in 5 cm^3 dry THF. To this mixture was slowly added a solution of *N*,*N*′-carbonyldiimidazole (9.38 mmol) in 15 cm^3 dry THF. The resulting suspension was intensively stirred for approximately 0.5 h in an ice bath. The mixture was then cooled to less than 5 °C, and 89% *tert*-butyl or *tert*-amyl hydroperoxide (11.05 mmol) was added. The progress of the reaction was monitored by means of TLC (mobile phase CH_2Cl_2/CH_3COCH_3 9:1; a solution of sodium iodide in acetic acid was used for visualisation of the separated peroxy substances). The reaction was allowed to proceed for 6 h, after which 18 cm^3 Et_2O was added and stirring was continued for an additional 20 min. The mixture was then washed with 25 cm^3 10% NaOH and with 25 cm^3 water. The organic layer was dried over anhydrous $MgSO_4$. Solutions of each asymmetrical azo-perester were separated from the drying agent and concentrated by rotary evaporation at room temperature. The crude dried products had an oily consistency. Further purification was conducted by column chromatography (silica gel as stationary phase and CH_2Cl_2 as eluent). The products *tert*-butyl 4-(*tert*-butylazo)-4-cyanoperoxypentanoate (**3a**), *tert*-butyl 5-(*tert*-butylazo)-5-cyanoperoxyhexanoate (**3b**), and 1,1-dimethylpropyl 6-(*tert*-butylazo)-6-cyanoperoxyheptanoate (**4c**) were obtained in crystalline form. All other asymmetrical compounds were obtained as oils.

4-(tert-Butylazo)-4-cyanopentanoic acid (**2a**)
Yield 66%; m.p.: 86–87 °C (Ref. [3]: m.p.: 79–81 °C).

5-(tert-Butylazo)-5-cyanohexanoic acid
(**2b**, $C_{11}H_{19}N_3O_2$)
Yield 68%; m.p.: 54–56 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 11.03$ (s, 1H, O*H*), 2.41–2.36 (t, $J = 7.2$ Hz, 2H, CH_2CO), 2.12–1.90 (m, 2H, CH_2), 1.82–1.72 (m, 2H, CH_2), 1.67–1.58 (m, 2H, CH_2), 1.55 (s, 3H, CH_3), 1.20 (s, 9H, (CH_3)$_3$C) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 179.01$ (*C*O), 119.33 (*C*N), 71.44 (*C*(CN)), 68.24 ((CH$_3$)*C*), 37.34 (*C*H$_2$), 33.36 (*C*H$_3$C(CN)), 26.55 ((*C*H$_3$)$_3$C), 23.76 (*C*H$_2$), 19.28 (*C*H$_2$) ppm; IR (CH_2Cl_2): $\bar{\nu} = 3{,}220$–$2{,}810$, 2,260, 1,715, 1,460, 1,365 cm^{-1}.

6-(tert-Butylazo)-6-cyanoheptanoic acid
(**2c**, $C_{12}H_{21}N_3O_2$)
Yield 62%; m.p.: 52–55 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 10.02$ (s, 1H, O*H*), 2.33–2.28 (t, $J = 7.5$ Hz, 2H, CH_2CO), 2.04–1.81 (m, 2H, CH_2), 1.66–1.09 (m, 4H, CH_2), 1.51 (s, 3H, CH_3), 1.16 (s, 9H, (CH_3)$_3$C) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 179.50$ (*C*O), 119.47 (*C*N), 71.58 (*C*(CN)), 68.07 ((CH$_3$)*C*), 37.74 (*C*H$_2$), 33.55 (*C*H$_3$C(CN)), 26.51 (*C*H$_2$), 24.18 ((*C*H$_3$)$_3$C), 23.80 (*C*H$_2$), 23.56 (*C*H$_2$) ppm; IR (CH_2Cl_2): $\bar{\nu} = 3{,}450$–$3{,}160$, 2,240, 1,740, 1,350 cm^{-1}.

tert-Butyl 4-(tert-butylazo)-4-cyanoperoxypentanoate (**3a**)
Yield 89%; m.p.: 59–61 °C (Ref. [9]: oil); ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 2.52$–2.31 (m, 2H, CH_2CO), 2.31–2.26 (m, 2H, CH_2), 1.54 (s, 3H, CH_3), 1.25 (s, 9H, (CH_3)$_3$C), 1.17 (s, 9H, (CH_3)$_3$C) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 169.52$ (*C*O), 118.79 (*C*N), 83.69 (*C*(CH$_3$)$_3$), 70.72 (*C*(CN)), 68.64 ((CH$_3$)*C*), 33.01 (*C*H$_2$), 26.63 (*C*H$_2$), 26.57 ((*C*H$_3$)$_3$C), 26.08 (*C*H$_2$), 23.79 (*C*H$_3$C(CN)) ppm; IR (CH_2Cl_2): $\bar{\nu} = 2{,}980$, 2,300, 1,785, 1,465, 1,365 cm^{-1}.

tert-Butyl 5-(tert-butylazo)-5-cyanoperoxyhexanoate
(**3b**, $C_{15}H_{27}N_3O_3$)
Yield 61%; m.p.: 39–43 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 2.33$–2.28 (t, $J = 7.2$ Hz, 2H, CH_2), 2.07–1.85 (m, 4H, CH_2), 1.50 (s, 3H, CH_3), 1.23 (s, 9H, (CH_3)$_3$C), 1.14 (s, 9H, (CH_3)$_3$C) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 169.94$ (*C*OO), 119.12 (*C*N), 83.26 (*C*(CH$_3$)$_3$), 71.21 (*C*(CN)), 37.19 (*C*H$_2$), 30.50 (*C*H$_2$), 26.39 ((*C*H$_3$)$_3$C), 25.39 ((CH$_3$)*C*), 23.65 (*C*H$_3$(C)CN), 19.52 (*C*H$_2$) ppm; IR (CH_2Cl_2): $\bar{\nu} = 2{,}975$, 2,240, 1,770, 1,465, 1,385 cm^{-1}.

tert-Butyl 6-(tert-butylazo)-6-cyanoperoxyheptanoate
(**3c**, $C_{16}H_{29}N_3O_3$)
Yield 80%; ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 2.2$–62.21 (t, $J = 7.5$ Hz, 2H, CH_2), 2.17–1.75 (m, 2H, CH_2), 1.64–1.57 (m, 2H, CH_2), 1.49–1.17 (m, 2H, CH_2), 1.47 (s, 3H, CH_3), 1.21 (s, 9H, C(CH_3)$_3$), 1.13 (s, 9H, C(CH_3)$_3$) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 170.33$ (*C*OO), 119.26 (*C*N), 83.09 (*C*(CH$_3$)$_3$), 71.43 (*C*(CN)), 37.58 (*C*H$_2$), 30.65 (*C*H$_2$), 26.38 ((*C*H$_3$)$_3$C), 24.37 (*C*H$_3$(C)CN), 23.67 (*C*H$_2$), 23.56 ((CH$_3$)*C*) ppm; IR (CH_2Cl_2): $\bar{\nu} = 2{,}990$, 2,250, 1,780, 1,480, 1,375 cm^{-1}.

1,1-Dimethylpropyl 4-(tert-butylazo)-4-cyanoperoxypentanoate (**4a**, $C_{15}H_{27}N_3O_3$)
Yield 85%; ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 2.46$–2.40 (m, 2H, CH_2), 2.28–2.22 (m, 2H, CH_2), 1.63–1.49 (m, 2H, CH_2), 1.55 (s, 3H, CH_3CCN), 1.20 (s, 6H, (CH_3)$_2$C), 1.18 (s, 9H, (CH_3)$_3$C), 0.92–0.84 (m, 3H, CH_3CH$_2$) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 169.47$ (*C*OO), 118.73 (*C*N), 85.99 (*C*(CH$_3$)$_2$C$_2$H$_5$), 70.68 (*C*(CN)), 68.58 ((CH$_3$)*C*), 32.93 (*C*H$_2$CH$_3$), 31.32 (*C*H$_2$), 26.49 (*C*H$_2$), 26.20 (*C*H$_2$), 23.73 ((*C*H$_3$)CCN), 23.63 (C(*C*H$_3$)$_2$C$_2$H$_5$), 8.15 (CH$_2$*C*H$_3$) ppm; IR (CH_2Cl_2): $\bar{\nu} = 2{,}970$, 2,250, 1,775, 1,445, 1,360 cm^{-1}.

1,1-Dimethylpropyl 5-(tert-butylazo)-5-cyanoperoxyhexanoate (**4b**, $C_{16}H_{29}N_3O_3$)
Yield 66%; ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 2.35$–2.30 (t, $J = 7.2$ Hz, 2H, CH_2CH$_3$), 2.11–1.87 (m, 2H, CH_2), 1.82–1.49 (m, 2H, CH_2), 1.53 (s, 3H, CH_3), 1.20 (s, 6H, (CH_3)$_2$C), 1.18 (s, 9H, (CH_3)$_3$C), 0.89–0.84 (t, $J = 7.5$ Hz, 3H, CH_3CH$_2$) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 169.93$ (*C*OO), 119.22 (*C*N), 85.67 (*C*(CH$_3$)$_2$C$_2$H$_5$), 71.29 (*C*(CN)), 68.22 ((CH$_3$)*C*), 37.27 (*C*H$_2$CH$_3$), 31.31 (*C*H$_2$), 30.66 (*C*H$_2$), 26.49 (*C*H$_2$), 23.74 (*C*H$_3$C(CN)), 23.62 (C(*C*H$_3$)$_2$C$_2$H$_5$), 19.61 (*C*H$_2$), 8.12 (CH$_2$*C*H$_3$) ppm; IR (CH_2Cl_2): $\bar{\nu} = 2{,}975$, 2,245, 1,765, 1,470, 1,375 cm^{-1}.

1,1-Dimethylpropyl 6-(tert-butylazo)-6-cyanoperoxyheptanoate (**4c**, $C_{17}H_{31}N_3O_3$)
Yield 85%; m.p.: 15–19 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 2.26$–2.21 (t, $J = 7.5$ Hz, 2H, CH_2CH$_3$), 1.97–1.83 (m, 2H, CH_2), 1.78–1.74 (m, 2H, CH_2), 1.64–1.40 (m, 4H, CH_2), 1.47 (s, 3H, CH_3), 1.15 (s, 6H, (CH_3)$_2$C), 1.13 (s, 9H, (CH_3)$_3$C), 0.84–0.79 (t, $J = 7.5$ Hz, 3H, CH_3CH$_2$) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 170.36$ (*C*OO), 119.25 (*C*N), 85.44 (*C*(CH$_3$)$_2$C$_2$H$_5$), 71.45 (*C*(CN)), 67.95 ((CH$_3$)*C*), 37.57 (*C*H$_2$CH$_3$), 31.19 (*C*H$_2$), 30.70 (*C*H$_2$), 26.36 (*C*H$_2$), 24.37 (*C*H$_3$C(CN)), 23.65 (C(*C*H$_3$)$_2$C$_2$H$_5$), 23.50 (*C*H$_2$), 23.22 (*C*H$_2$), 8.07 (CH$_2$*C*H$_3$) ppm; IR (CH_2Cl_2): $\bar{\nu} = 2{,}970$, 2,245, 1,775, 1,470, 1,375 cm^{-1}.

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