A New Approach to the Synthesis of Vicinal Iodoperoxyalkanes by the Reaction of Alkenes with Iodine and Hydroperoxides

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Received 24 April 2007; revised 12 July 2007

Abstract: A convenient procedure was developed for the synthesis of vicinal iodoperoxyalkanes by the reaction of alkenes with iodine and hydroperoxides. The best results were achieved with the use of excess iodine. The replacement of one iodine atom by hydroperoxides in vicinal diiodoalkanes was discovered. A suggestion was made about the reaction mechanism.

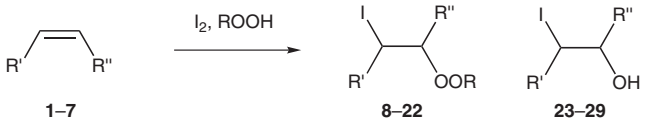
Key words: iodination, peroxidation, hydrogen peroxide, *tert*-butyl hydroperoxide, iodoperoxyalkanes

In recent years, organic peroxides and methods for their synthesis have attracted considerable interest, particularly, after the discovery of antimalarial activity of compounds belonging to this class,[1] tetraoxanes and ozonides, showing stronger activity. The presence of the peroxide fragment in artemisinin, which is used for the treatment of malaria,[2] is of importance. A series of more recent studies in this field were concerned with a search for simple analogues of artemisinin.[3]

Natural peroxides, such as plakinic acid E and its structural analogues isolated from *Plakortis sp.*, have cytotoxic activity against some types of tumor cells,[4] which has attracted attention to the chemistry of 1,2-dioxolanes.[5] In industry, organic peroxides are still of importance as radical polymerization initiators and oxidizing agents.[6] The above-mentioned practical aspects of the use of peroxides stimulated the development of new methods for their synthesis.

In this study, we performed a simple synthesis of peroxides containing iodine and the peroxy group in the vicinal position. Earlier, iodoperoxyalkanes had been prepared by peroxymercuration of alkenes followed by iodination,[7] and by the reaction of alkenes with 1,3-diiodo-5,5-dimethylhydantoin and hydrogen peroxide.[8] Cyclic iodoperoxides, which are of interest for the design of new antimalarial drugs, were synthesized primarily by intramolecular cyclization of hydroperoxyalkenes with the use of bis(collidine)iodine hexafluorophosphate,[9] NIS,[9c,10] potassium hydride (or *tert*-butoxide) or pyridine and iodine[10c,11] and, with worse results, with the use of only iodine.[12] Related vicinal iodomonoperoxyacetals were synthesized by the reaction of enol esters with NIS and *t*-BuOOH.[13] Since iodoperoxides contain iodine, which is easy to replace, these compounds are valuable reagents in preparative nucleophilic substitution reactions occurring with retention of the peroxide fragment. This may find use in the synthesis of biologically active compounds.

The proposed method for the synthesis of iodoperoxyalkanes is based on the reaction of alkenes with iodine and hydroperoxides (Scheme 1). The reactions were completed in 3 hours (with hydrogen peroxide), 5 hours (with *tert*-butyl hydroperoxide), and 72 hours (with tetrahydropyranyl hydroperoxide) at room temperature by mixing alkenes **1**–**7**, excess iodine, and hydroperoxide in diethyl ether or dichloromethane. Iodoperoxyalkanes **8**–**22** were synthesized in yields of up to 70%. Iodohydroxyalkanes **23**–**29** were obtained as by-products.



1–7 **8–22** **23–29**

1, **8**, **15**, **15'**, **19**, **23** R' = H, R'' = *n*-Bu;
2, **9**, **24** R' = H, R'' = *n*-C_5H_{11};
3, **10**, **25** R' = H, R'' = *n*-C_8H_{17};
4, **11**, **26** R' = H, R'' = *n*-$C_8H_{16}COOMe$;
5, **12**, **16**, **20**, **27** R', R'' = - C_3H_6 -;
6, **13**, **17**, **21**, **28** R', R'' = - C_4H_8 -;
7, **14**, **18**, **22**, **29** R', R'' = - C_6H_{12} -
8–14 R = *t*-Bu; **15–18** R = H; **19–22** R =

Scheme 1 Synthesis of iodoperoxyalkanes

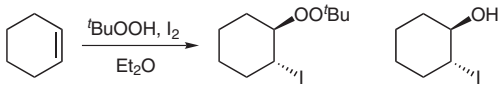
Tables 1 and 2 present the influence of the reagent ratio on the selectivity of iodoperoxidation of alkanes, as exemplified by the reaction of cyclohexene (**6**) with an I_2-*tert*-butyl hydroperoxide system. The most interesting result obtained in a series of experiments is that an increase in the excess amount of iodine leads to an increase, though only slight, in the yield of 1-(*tert*-butylperoxy)-2-iodocyclohexane (**13**) and a decrease in the amount of 2-iodocyclohexanol (**28**) by a factor of more than 2.5 (Table 1), whereas vicinal diiodoalkane is produced in trace amounts.

An increase in the amount of *t*-BuOOH from 1.2 to 5 moles per mole of alkene allows an increase in the selectivity of the synthesis (the **13**:**28** ratio increases from 1.24 to 2.9, see Table 2).

The chromatographic monitoring of the conversion of cyclohexene during the course of the reaction was inefficient

SYNTHESIS 2007, No. 19, pp 2979–2986
Advanced online publication: 11.09.2007
DOI: 10.1055/s-2007-990776; Art ID: P05007SS

Table 1 Influence of the Amount of I_2 on the Yield of **13** and **28**[a]



6 **13** **28**

Moles of I_2 per mole of **6**	0.5	0.7	1	2
Yield (%) of **13**[b]	54	61	65	70
Yield (%) of **28**[b]	31	22	18	12
Yield ratio **13**:**28**	1.74	2.77	3.61	5.83

[a] Reaction conditions: A 50% *t*-BuOOH solution (2.63 g, 14.6 mmol) in Et_2O, I_2 (0.48–1.86 g, 1.88–7.32 mmol), and **6** (0.3 g, 3.66 mmol) were successively added to Et_2O (5 mL). The homogeneous mixture was kept at 20–25 °C for 5 h.
[b] Yield based on the isolated product.

Table 2 Influence of the Amount of *t*-BuOOH on the Molar Ratio of **13** and **28**[a] (cf. Table 1)

Moles of *t*-BuOOH per mole of **6**	1.2	2.5	4	5
Molar ratio **13**:**28**[b]	1.24	2.13	2.8	2.9

[a] Reaction conditions: A 50% *t*-BuOOH solution (0.79–3.29 g, 4.39–18.3 mmol) in Et_2O, I_2 (0.65 g, 2.56 mmol), and **6** (0.3 g, 3.66 mmol) were successively added to Et_2O (5 mL). The homogeneous mixture was kept at 20–25 °C for 5 h.
[b] ^{1}H NMR spectroscopic data.

because of the volatility of this compound and the presence of peroxides and iodine in the tested samples.

Vicinal *tert*-butylperoxyiodoalkanes **8**–**14** (Table 3, entries 1–7) and hydroperoxyiodoalkanes **15**–**18** (entries 8–11) were synthesized from alkenes using the above-mentioned reagent ratios. 2-Hydroperoxytetrahydropyran is characterized by lower reactivity compared to hydrogen peroxide and *tert*-butyl hydroperoxide. Hence, the reaction time required for the preparation of vicinal tetrahydropyranylperoxyiodoalkanes **19**–**22** (entries 12–15) was increased to 72 hours (Table 3).

Peroxides **8**–**14** and **19**–**22** can be easily isolated in pure state by column chromatography. The isolation of hydroperoxides **15**–**18** in the reaction with iodine (0.7 mol per mole of alkene) and *t*-BuOOH (4 mol per mole of alkene) presented difficulties, and these compounds were obtained as mixtures with substantial amounts of iodoalkanols **23** and **27**–**29**. Iodohydroperoxides **15**–**18** and the corresponding iodoalkanols **23** and **27**–**29** differ in R_f by only 0.03–0.08. The characteristic signals of the hydrogen atoms in the ^{1}H NMR spectra for C*H*OOH are shifted downfield by more than 0.2 ppm compared to C*H*OH, which allowed us to determine the yields of **15**–**18** from the ^{1}H NMR spectroscopic data. Iodohydroperoxides **15**–**18** were isolated in individual state by column chromatography after the reaction with excess iodine (4 mol per mole of alkene). Under these conditions, the formation of iodoalkanols was substantially suppressed. The drawback of this method for the synthesis of iodoperoxides is that it is difficult to remove the large excess of unconsumed iodine.

Table 3 Vicinal *tert*-Butylperoxyiodoalkanes **8**–**14**, Hydroperoxyiodoalkanes **15**–**18**, and Tetrahydropyranylperoxyiodoalkanes **19**–**22** Prepared[a]

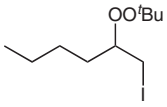
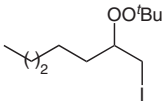
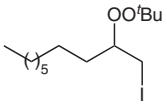
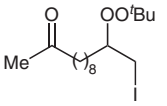
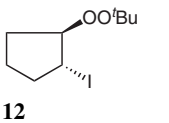
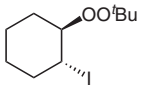
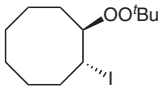
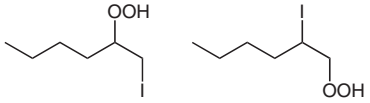
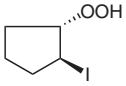
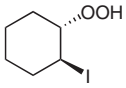
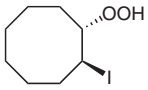
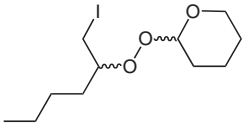
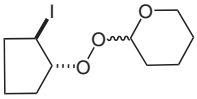
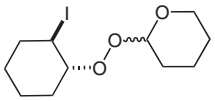
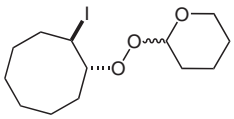
Entry	Alkene	Iodoperoxide	Yield (%)
1	Hex-1-ene (**1**)	 **8**	57
2	Hept-1-ene (**2**)	 **9**	52
3	Dec-1-ene (**3**)	 **10**	61
4	Methyl undec-10-enoate (**4**)	 **11**	53
5	Cyclopentene (**5**)	 **12**	68

Table 3 Vicinal *tert*-Butylperoxyiodoalkanes **8**–**14**, Hydroperoxyiodoalkanes **15**–**18**, and Tetrahydropyranylperoxyiodoalkanes **19**–**22** Prepared[a] (continued)

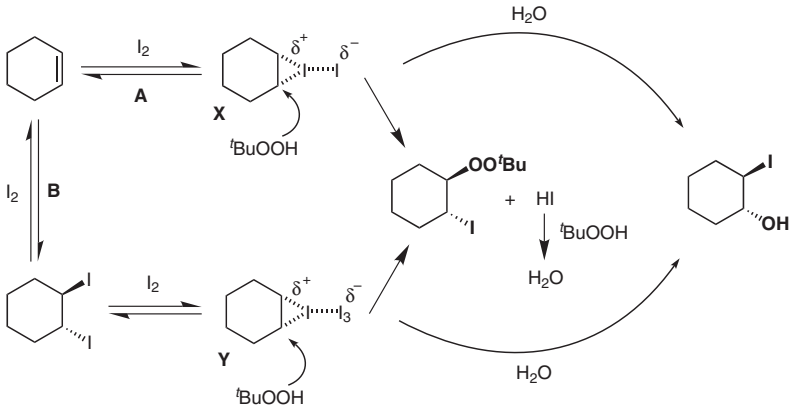
Entry	Alkene	Iodoperoxide	Yield (%)
6	Cyclohexene (**6**)	 **13**	61
7	Cyclooctene (**7**)	 **14**	67
8	Hex-1-ene (**1**)	 **15** + **15′**	62,[b] 63[c]
9	Cyclopentene (**5**)	 **16**	59,[b] 61[c]
10	Cyclohexene (**6**)	 **17**	61,[b] 62[c]
11	Cyclooctene (**7**)	 **18**	43,[b] 51[c]
12	Hex-1-ene (**1**)	 **19**	31
13	Cyclopentene (**5**)	 **20**	47
14	Cyclohexene (**6**)	 **21**	51
15	Cyclooctene (**7**)	 **22**	37

[a] General reaction conditions: 0.7 mol of I_2 per mole of alkene, 4 mol of hydroperoxide per mole of alkene; reaction time: 5 h (**8**–**14**), 3 h (**15**–**18**), and 72 h (**19**–**22**); temperature: 20–25 °C. Yield based on isolated product, exept where otherwise specified.
[b] Yield from ^{1}H NMR spectroscopic data.
[c] 4 mol of I_2 per mole of alkene; yield based on the isolated product.

The reaction of hydrogen peroxide with hex-1-ene produced a mixture of regioisomers of iodoperoxides **15** and **15′** (entry 8).

2-Tetrahydropyranylperoxy-1-iodoalkanes were isolated as mixtures of diastereomers. The ^{13}C NMR spectra of these mixtures show double sets of signals. The separation of the mixtures presents difficulties because of similar R_f and the tendency of iodoperoxides to undergo decomposition.

The reactions of all hydroperoxides afforded also vicinal iodoalkanols as by-products in yields from ~10 to 40%. In most cases, these by-products were not isolated and were



Scheme 2 Proposed mechanism of formation of iodoperoxyalkanes and iodoalkanols.

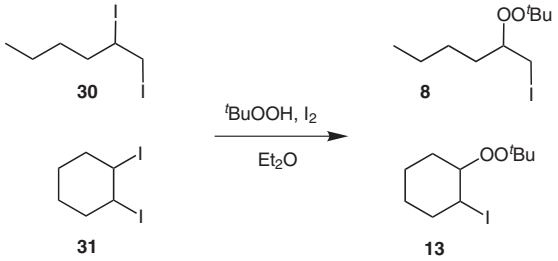
identified in mixtures with iodoperoxyalkanes based on the characteristic signals in the ^{13}C and ^{1}H NMR spectra and by TLC comparison with iodoalkanols, which were prepared according to known procedures.[14] In the syntheses of iodoperoxides **12**,**13**,**20**, and **21**, the yields of iodoalkanols **27** and **28** were 28, 26, 17, and 15%, respectively, based on the isolated products. In the synthesis of iodoperoxide **11**, iodoalkanol **26** was isolated in 33% yield. Virtually the same result was obtained in the synthesis of **13** in dichloromethane.

We propose the following mechanism of formation of iodoperoxyalkanes and iodoalkanols (Scheme 2). Apparently, iodoperoxyalkane is formed by two pathways, **A** and **B**. The pathway **A** corresponds to the classical scheme of the successive addition of electrophilic iodine and nucleophilic hydroperoxide to the double bond.

The pathway **B** is an original hypothesis of the present study. It is based on experimental data, according to which an increase in the amount of iodine (a nucleophile competing with *tert*-butyl hydroperoxide) leads to an increase in the yield of 1-(*tert*-butylperoxy)-2-iodocyclohexane (**13**), whereas the expected 1,2-diiodocyclohexane (**31**) is formed in trace amounts (Table 1). Apparently, iodoperoxide is formed by the pathway **B** as a result of the previously unknown process. Initially, the reaction produces 1,2-diiodocyclohexane (**31**) (diiodides are known to be in equilibrium with iodine and alkene[15]), which is transformed under the action of iodine into intermediate **Y** containing a partially positive charge on the carbon atoms. The latter reacts with hydroperoxide.

To confirm this hypothesis, authentic 1,2-diiodohexane (**30**) and 1,2-diiodocyclohexane (**31**) were introduced into the reaction with *tert*-butyl hydroperoxide. The reactions were carried out in the absence and in the presence of iodine (Scheme 3, Table 4).

It can be seen that iodine actively catalyzes the replacement of one iodine atom in diiodoalkanes by *tert*-butyl hydroperoxide. In the absence of iodine, the reaction virtually does not proceed. In the presence of 0.5 mol of I_2 per mole of alkene, iodoperoxides **8** and **13** were obtained in 67 and 70% yield, respectively.



Scheme 3 Synthesis of iodoperoxyalkanes from diiodoalkanes.

Table 4 Synthesis of Vicinal *tert*-Butylperoxyiodoalkanes from Vicinal Diiodoalkanes[a]

Iodoperoxide	Moles of I_2 per mole of diiodoalkane **30** or **31**		
	without I_2	0.1	0.5
Yield (%) of **8**[c]	traces	29	67
Yield (%) of **13**[b,c]	15	41	70

[a] Reaction conditions: A 50% *t*-BuOOH solution (3.6 g, 20 mmol) in Et_2O, I_2 (0.13 or 0.64 g, 0.5 or 2.5 mmol), and diiodoalkane (5 mmol) were successively added to Et_2O (5 mL). The mixture was kept at 20–25 °C for 2 h.

[b] The formation of **13** in the reaction in the absence of I_2 is apparently attributed to the fact that we failed to prepare 1,2-diiodocyclohexane (**31**) not contaminated with I_2; compound **31** partially decomposes in the course of isolation with elimination of I_2.

[c] Yield based on the isolated product.

Attempts to replace iodine by the *tert*-butylperoxy group in structurally similar halogen-containing compounds, such as iodocyclohexane, 2-iodocyclohexanol (**28**), and 1,2-dibromocyclohexane, in the presence of iodine (0.5 mol per mole of halide) failed. Hence, the above-described reaction is characteristic of vicinal diiodo derivatives.

We failed to perform iodoperoxidation of allyl propionate by *tert*-butyl hydroperoxide; instead, we obtained a diiodination product of the double bond. Iodine was also not replaced by *tert*-butyl hydroperoxide in the separately prepared diiodination product of allyl propionate. Apparently, this is associated with the ability of the carbonyl ox-

ygen atom to compensate the partially positive charge in intermediates **X** and **Y** through the cyclic transition state.

Iodoalkanols are, apparently, generated as a result of the addition of water to intermediates **X** and **Y**. In turn, water is formed upon oxidation of HI with *t*-BuOOH (Scheme 2). Iodoalkanols are not formed by reduction of iodoperoxides under the reaction conditions (under the action of iodine) or in the course of their isolation, which was confirmed by the corresponding experiments with the separately prepared iodoperoxide, which remained unconsumed. It cannot be completely ruled out that a small amount of iodoalkanol is generated due to the presence of residual water in hydroperoxide solutions.

We performed an experiment on the determination of the competitive influence of *tert*-butyl hydroperoxide and water in iodoperoxidation of cyclohexene. In a *t*-BuOOH/H_2O/I_2/alkene system (the molar ratio was 8:2:0.7:1), iodoperoxide **13** and iodoalkanol **28** were obtained in a ratio of 1.05 (^{1}H NMR spectroscopic data). The results of the experiment allow a conclusion that *tert*-butyl hydroperoxide, which is traditionally considered as a stronger nucleophile than water, is less reactive than the latter in the process under consideration.

Iodoperoxides were isolated according to an original procedure based on removal of an iodine residue through the formation of the KI·I_2 complex by washing the reaction mixture with a KI solution. In this case, a standard procedure for removal of iodine with $Na_2S_2O_5$ is unsuitable because it leads to reduction of iodoperoxides to iodoalkanols.

To summarize, we have developed a simple procedure for the synthesis of vicinal iodoperoxides by the reaction of alkenes with iodine and hydroperoxides, which enables the preparation of the target compounds in yields of up to 70%. The reaction of vicinal diiodides with hydroperoxides was discovered. In the presence of iodine, only one iodine atom is replaced by the peroxy group to form vicinal iodoperoxides. A mechanism has been suggested for this reaction.

NMR spectra were recorded on Bruker AC-200 (200.13 MHz for ^{1}H, 50.32 MHz for ^{13}C), Bruker WM-250 (250.13 MHz for ^{1}H, 62.9 MHz for ^{13}C), and Bruker AM-300 (300.13 MHz for ^{1}H, 75.4 MHz for ^{13}C) spectrometers in $CDCl_3$. Analytical TLC: Silufol UV-254, Silpearl as the sorbent, starch as the binder. Chromatography was performed on silica gel (63–200 mesh, Merck). Alkenes, allyl propionate, $Na_2S_2O_5$, 70% aq *t*-BuOOH, and KI were purchased from Acros. THF, hexane, Et_2O, EtOAc, I_2, and 37% aq H_2O_2 (all of reagent grade) were used without additional purification. Solutions of *t*-BuOOH in Et_2O and CH_2Cl_2 and a solution of H_2O_2 in Et_2O were prepared by extraction of the corresponding peroxides from their aqueous solutions followed by drying over $MgSO_4$.[16] The concentration of peroxides was determined by titration.[17] Iodocyclohexane,[18] 1,2-dibromocyclohexane,[19] tetrahydro-2*H*-pyran-2-yl hydroperoxide,[20] and diiodoalkanes **30**[21] and **31**[22] were prepared according to known procedures.

Iodocyclohexane[18]
^{1}H NMR (250.13 MHz, $CDCl_3$): δ = 1.26–2.25 (m, 10 H, CH_2), 4.30–4.44 (m, 1 H, CHI).

1,2-Dibromocyclohexane[19]
^{1}H NMR (250.13 MHz, $CDCl_3$): δ = 1.42–1.59 (m, 2 H, CH_2), 1.63–1.97 (m, 4 H, CH_2), 2.36–2.55 (m, 2 H, CH_2), 4.39–4.52 (m, 2 H, CHI).

1,2-Diiodohexane (30)[21]
^{1}H NMR (250.13 MHz, $CDCl_3$): δ = 0.93 (t, *J* = 7.1 Hz, 3 H, CH_3), 1.20–2.01 (m, 6 H, CH_2), 3.67 (dd, *J* = 9.85, 3.94 Hz, 1 H, CH_2I), 4.05 (dd, *J* = 9.85, 11.81 Hz, 1 H, CH_2I), 4.27–4.38 (m, 1 H, CHI).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 13.8, 13.9 (CH_2I, CH_3), 21.7 (CH_2CH_3), 30.9 ($CH_2CH_2CH_3$), 33.3 (CHI), 38.7 (CH_2CHI).

1,2-Diiodocyclohexane (31)[22]
^{1}H NMR (250.13 MHz, $CDCl_3$): δ = 1.30–2.39 (m, 8 H, CH_2), 4.95–5.07 (m, 2 H, CHI).

1-*tert*-Butylperoxy-2-iodoalkanes 8–14; General Procedures
A 50% *t*-BuOOH solution (1.2–5 mol per mole of alkene) in Et_2O, I_2 (0.5–2 mol per mole of alkene), and the appropriate alkene (0.3 g) were successively added to Et_2O (5 mL). The homogeneous mixture was kept at 20–25 °C for 5 h. Then hexane (40 mL) was added, and the mixture was successively washed with H_2O (2 × 10 mL) and aq 10% KI (7 × 10 mL) until the mixture became slightly colored, and again with H_2O (2 × 10 mL). Then the mixture was dried ($MgSO_4$) and filtered. The filtrate was concentrated in vacuum (~10 mm Hg) at a temperature not higher than 30 °C. Peroxides **8**–**14** were isolated in individual state by silica gel chromatography using hexane–EtOAc (30:1) as eluent. The iodohydroxyalkane by-products were isolated by silica gel chromatography using hexane–EtOAc (5:1) as eluent.

The synthesis of **13** was carried out using CH_2Cl_2 (5 mL) and a 30% *t*-BuOOH solution in CH_2Cl_2.

Iodoperoxidation of allyl propionate was carried out analogously; *t*-BuOOH (4 mol per mole of allyl propionate) and I_2 (0.7 mol per mole of allyl propionate) were used, the reaction time was 5 h. 2,3-Diiodopropyl propionate was isolated.

The formation of iodoalkanols by reduction of iodoperoxides with I_2 under the reaction conditions or during isolation was determined by adding authentic 1-*tert*-butylperoxy-2-iodocyclohexane (0.3 g) instead of the alkene to the reaction mixture or by isolating 1-*tert*-butylperoxy-2-iodocyclohexane by working up its solution (0.3 g) in Et_2O (10 mL) according to the procedure used for the isolation of peroxides **8**–**14**.

2-(*tert*-Butylperoxy)-1-iodohexane (8)[23]
Slightly yellow oil; R_f = 0.34 (TLC, hexane–EtOAc, 20:1).

^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 7 Hz, 3 H, CH_3), 1.14–1.71 (m, 15 H, CH_2), 3.27 (dd, *J* = 10, 6.6 Hz, 1 H, CH_2I), 3.43 (dd, *J* = 10, 3.4 Hz, 1 H, CH_2I), 3.69–3.78 (m, 1 H, CH).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 9.1 (CH_2I), 13.9 (CH_3CH_2), 26.5 (CH_3C), 22.5, 27.5, 32.1 (CH_2), 80.1 (CO), 81.8 (CHO).

2-(*tert*-Butylperoxy)-1-iodoheptane (9)
Slightly yellow oil; R_f = 0.41 (TLC, hexane–EtOAc, 20:1).

^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 7 Hz, 3 H, CH_3), 1.18–1.69 (m, 17 H, CH_2), 3.28 (dd, *J* = 10, 6.6 Hz, 1 H, CH_2I), 3.43 (dd, *J* = 10, 3.5 Hz, 1 H, CH_2I), 3.69–3.81 (m, 1 H, CH).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 9.0 (CH_2I), 13.9 (CH_3CH_2), 26.6 (CH_3C), 22.5, 25.0, 31.7, 32.5 (CH_2), 80.1 (CO), 81.9 (CHO).

Anal. Calcd for $C_{11}H_{23}IO_2$: C, 42.05; H, 7.38; I, 40.39. Found: C, 42.12; H, 7.77; I, 40.65.

2-(*tert*-Butylperoxy)-1-iododecane (10)
Slightly yellow oil; R_f = 0.54 (TLC, hexane–EtOAc, 20:1).

^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 0.87 (t, *J* = 7 Hz, 3 H, CH_3), 1.14–1.69 (m, 23 H, CH_2), 3.30 (dd, *J* = 10, 6.6 Hz, 1 H, CH_2I), 3.45 (dd, *J* = 10, 3.5 Hz, 1 H, CH_2I), 3.69–3.81 (m, 1 H, CH).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 9.2 (CH_2I), 14.1 (CH_3CH_2), 26.5 (CH_3C), 22.6, 25.4, 29.2, 29.4, 29.5, 31.8, 32.5 (CH_2), 80.3 (CO), 81.9 (CHO).

Anal. Calcd for $C_{14}H_{29}IO_2$: C, 47.20; H, 8.20; I, 35.62. Found: C, 47.33; H, 8.09; I, 35.17.

Methyl 10-(*tert*-Butylperoxy)-11-iodoundecanoate (11)
Slightly yellow oil; R_f = 0.74 (TLC, hexane–EtOAc, 5:1).

^{1}H NMR (250.13 MHz, $CDCl_3$): δ = 1.15–1.65 (m, 23 H, CH_2, CH_3), 2.27 (m, *J* = 7.5 Hz, 2 H, CH_2CO_2Me), 3.28 (dd, *J* = 9.9, 6.6 Hz, 1 H, CH_2I), 3.43 (dd, *J* = 9.9, 3.3 Hz, 1 H, CH_2I), 3.63 (s, 3 H, OCH_3), 3.67–3.77 (m, 1 H, CHO).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 9.2 (CH_2I), 26.5 (CH_3C), 24.9, 25.3, 29.0, 29.1, 29.3, 32.4, 34.9 (CH_2), 51.4 (OCH_3), 80.3 (CO), 81.9 (CHO), 174.2 (CO_2Me).

Anal. Calcd for $C_{16}H_{31}IO_4$: C, 46.38; H, 7.54; I, 30.63. Found: C, 45.98; H, 7.36; I, 30.81.

2-(*tert*-Butylperoxy)-1-iodocyclopentane (12)
Slightly yellow oil; R_f = 0.31 (TLC, hexane).

^{1}H NMR (250.13 MHz, $CDCl_3$): δ = 1.20 (s, 9 H, CH_3), 1.45–2.24 (m, 6 H, CH_2), 4.55–4.60 (m, 1 H, CHO), 4.73–4.78 (m, 1 H, CHI).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 26.4 (CH_3), 22.6, 27.5, 31.4, 35.8 (CH_2, CHI), 80.2 (CO), 92.7 (CHO).

Anal. Calcd for $C_9H_{17}IO_2$: C, 38.04; H, 6.03; I, 44.66. Found: C, 38.44; H, 6.32; I, 44.42.

2-(*tert*-Butylperoxy)-1-iodocyclohexane (13)
Slightly yellow oil; R_f = 0.33 (TLC, hexane).

^{1}H NMR (250.13 MHz, $CDCl_3$): δ = 1.25 (s, 9 H, CH_3), 1.30–2.39 (m, 8 H, CH_2), 3.94–4.04 (m, 1 H, CHO), 4.21–4.32 (m, 1 H, CHI).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 26.5 (CH_3), 22.6, 25.9, 29.1, 30.7, 36.0 (CH_2, CHI), 80.4 (CO), 84.4 (CHO).

Anal. Calcd for $C_{10}H_{19}IO_2$: C, 40.28; H, 6.42; I, 42.56. Found: C, 40.32; H, 6.80; I, 42.88.

1-(*tert*-Butylperoxy)-2-iodocyclooctane (14)
Slightly yellow oil; R_f = 0.39 (TLC, hexane).

^{1}H NMR (250.13 MHz, $CDCl_3$): δ = 1.15–2.21 (m, 21 H, CH_2, CH_3), 4.19–4.33 (m, 2 H, CHO, CHI).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 26.7 (CH_3), 25.1, 25.6, 26.4, 26.9, 30.1, 32.4, 35.4 (CH_2, CHI), 80.0 (CO), 89.4 (CHO).

MS (EI, 70 eV): *m*/*z* (%) = 326 ([M]$^+$, 1), 237 ([M – *t*-BuOO]$^+$, 63), 127 ([I]$^+$, 17), 109 ([M – *t*-BuOO – HI]$^+$, 61), 73 ([*t*-BuO]$^+$, 69), 57 ([*t*-Bu – H]$^+$, 100).

Anal. Calcd for $C_{12}H_{23}IO_2$: C, 44.18; H, 7.11; I, 38.90. Found: C, 44.78; H, 7.35; I, 38.54.

2,3-Diiodopropyl Propionate
Slightly red oil.

^{1}H NMR (250.13 MHz, $CDCl_3$): δ = 1.13 (t, *J* = 7.8 Hz, 3 H, CH_3), 2.36 (q, *J* = 7.8 Hz, 2 H, CH_2), 3.69 (dd, *J* = 10.5, 10.4 Hz, 1 H, CH_2I), 3.86 (dd, *J* = 10.5, 3.9 Hz, 1 H, CH_2I), 4.28–4.46 (m, 3 H, CHI, CH_2).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 8.2, 9.0 (CH_2I, CH_3), 24.8, 27.3 (CH_2CH_3, CHI), 67.9 (CH_2O), 173.2 (C=O).

Anal. Calcd for $C_6H_{10}I_2O_2$: C, 19.59; H, 2.74; I, 68.98. Found: C, 19.39; H, 2.47; I, 68.71.

2-Iodohexan-1-ol (23)[14a]
R_f = 0.5 (TLC, hexane–EtOAc, 4:1).

^{1}H NMR (250.13 MHz, $CDCl_3$): δ = 0.82–0.95 (t, *J* = 7 Hz, 3 H, CH_3), 1.22–1.64 (m, 6 H, CH_2), 2.12–2.27 (br s, 1 H, OH), 3.20 (dd, *J* = 9.8, 6.7 Hz, 1 H, CH_2I), 3.37 (dd, *J* = 9.8, 3.3 Hz, 1 H, CH_2I), 3.42–3.54 (m, 1 H, CHO).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 13.9 (CH_3), 16.5, 22.5, 27.7, 36.2 (CH_2, CH_2I), 70.9 (CHO).

Methyl 10-Hydroxy-11-iodoundecanoate (26)[24]
White crystals; mp 40.5–42 °C (Lit.[24] mp 43–44 °C); R_f = 0.25 (TLC, hexane–EtOAc, 5:1).

^{1}H NMR (250.13 MHz, $CDCl_3$): δ = 1.24–1.66 (m, 14 H, CH_2), 2.29 (m, *J* = 7.2 Hz, 2 H, CH_2CO_2Me), 1.87–1.99 (br s, 1 H, OH), 3.21 (dd, *J* = 10.1, 6.7 Hz, 1 H, CH_2I), 3.43 (dd, *J* = 10.1, 3.3 Hz, 1 H, CH_2I), 3.44–3.54 (m, 1 H, CHO), 3.65 (s, 3 H, OCH_3).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 16.6 (CH_2I), 24.9, 25.6 (CH_2), 29.1–29.3 (4 CH_2), 34.0, 36.6 (CH_2), 51.4 (OCH_3), 71.0 (CHOH), 174.2 (CO_2Me).

Anal. Calcd for $C_{12}H_{23}IO_3$: C, 42.12; H, 6.77; I, 37.08. Found: C, 42.37; H, 7.02; I, 37.28.

2-Iodocyclopentanol (27)[14a]
^{1}H NMR (250.13 MHz, $CDCl_3$): δ = 1.44–1.62 (m, 1 H, CH_2), 1.69–1.86 (m, 2 H, CH_2), 1.92–2.16 (m, 2 H, CH_2), 2.22–2.41 (m, 1 H, CH_2), 2.67–2.80 (s, 1 H, OH), 3.95–4.06 (m, 1 H, C*H*OH), 4.34–4.48 (m, 1 H, CHI).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 22.0, 31.0, 34.1 (CH_2), 35.6 (CHI), 82.0 (CHOH).

2-Iodocyclohexanol (28)[14a]
^{1}H NMR (250.13 MHz, $CDCl_3$): δ = 1.28–2.51 (m, 8 H, CH_2), 2.55–2.70 (s, 1 H, OH), 3.53–3.67 (m, 1 H, C*H*OH), 3.92–4.06 (m, 1 H, CHI).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 24.2, 27.7, 33.6, 38.4 (CH_2), 42.8 (CHI), 75.6 (CHOH).

2-Iodocyclooctanol (29)[14b]
^{1}H NMR (250.13 MHz, $CDCl_3$): δ = 1.25–2.33 (m, 13 H, CH_2, OH), 4.00–4.14 (m, 1 H, C*H*OH), 4.41–4.51 (m, 1 H, CHI).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 25.4, 25.9, 26.9, 32.4, 34.3, 42.0 (CH_2), 50.2 (CHI), 78.2 (CHOH).

1-Hydroperoxy-2-iodoalkanes 15–18 and Terahydro-2*H*-pyran Derivatives 19–22; General Procedure
I_2 (0.7 or 4 mol per mole of alkene) was dissolved in a 5–6% ethereal solution of H_2O_2 or tetrahydro-2*H*-pyran-2-yl hydroperoxide (4 mol per mole of alkene) and the appropriate alkene (0.3 g) was added at 20–25 °C. The homogeneous mixture was allowed to stand for 3 h (**15**–**18**) or 72 h (for **19**–**22**). Hexane (40 mL for **19**–**22**) or Et_2O (70 mL for **15**–**18**) was added, and the mixture was successively washed with H_2O (2 × 10 mL) and aq 10% KI (7 × 10 mL) until the mixture became slightly colored, and again with H_2O (2 × 10 mL). Then the mixture was dried ($MgSO_4$) and filtered. The filtrate was concentrated under vacuum (~10 mm Hg) at a temperature not higher than 30 °C. Peroxides were isolated by silica gel chromatography using hexane–EtOAc (5:1) (**15**–**18**) or hexane–EtOAc (30:1) (**19**–**22**) as eluent.

Mixture of 1-Hydroperoxy-2-iodohexane (15) and 2-Hydroperoxy-1-iodohexane (15′)
Slightly yellow oil; R_f = 0.54–0.56 (TLC, hexane–EtOAc, 4:1).

^{1}H NMR (250.13 MHz, $CDCl_3$): δ = 0.83–1.1 (m, 3 H, CH_3), 1.17–1.69 (m, 6 H, CH_2), 3.40–4.30 (m, 3 H, CH_2I, CHI, CH_2OO, CHOO), 7.90–8.00 (br s, 1 H, OOH).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 8.5 (CH_2I), 13.9 (CH_3), 20.0, 22.4, 27.5, 31.5, 31.7, 35.7, 41.5 (CH_2, CHI), 83.4, 81.7 (COO).

Anal. Calcd for $C_6H_{13}IO_2$: C, 29.53; H, 5.37; I, 51.99. Found: C, 29.93; H, 5.65; I, 51.62.

(*E*)-1-Hydroperoxy-2-iodocyclopentane (16)
Slightly yellow oil; R_f = 0.42 (TLC, hexane–EtOAc, 4:1).

^{1}H NMR (250.13 MHz, $CDCl_3$): δ = 1.25–2.27 (m, 6 H, CH_2), 4.56–4.64, 4.82–4.89 (m, 2 H, CH), 8.05–9.45 (br s, 1 H, OOH).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 22.7, 27.7, 29.6, 35.9 (CH_2, CHI), 95.0 (CHO).

Anal. Calcd for $C_5H_9IO_2$: C, 26.34; H, 3.98; I, 55.65. Found: C, 26.69; H, 4.22; I, 55.31.

(*E*)-1-Hydroperoxy-2-iodocyclohexane (17)
Slightly yellow oil; R_f = 0.46 (TLC, hexane–EtOAc, 4:1).

^{1}H NMR (250.13 MHz, $CDCl_3$): δ = 1.05–2.45 (m, 8 H, CH_2), 3.85–3.98, 4.21–4.33 (m, 2 H, CH), 8.90–9.40 (br s, 1 H, OOH).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 22.7, 25.8, 28.6, 30.7, 36.2 (CH_2, CHI), 86.3 (CHO).

MS (EI, 70 eV): *m*/*z* (%) = 242 ($[M]^+$, 3), 224 ($[M – H_2O]^+$, 8), 127 ($[I]^+$, 10), 115 ($[M – I]^+$, 13), 41 (100).

Anal. Calcd for $C_6H_{11}IO_2$: C, 29.77; H, 4.58; I, 52.43. Found: C, 30.19; H, 4.87; I, 52.63.

(*E*)-1-Hydroperoxy-2-iodocyclooctane (18)
Slightly yellow oil; R_f = 0.5 (TLC, hexane–EtOAc, 5:1).

^{1}H NMR (250.13 MHz, $CDCl_3$): δ = 1.15–2.48 (m, 12 H, CH_2), 4.22–4.48 (m, 2 H, CH), 8.20–8.65 (br s, 1 H, OOH).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 25.1, 25.4, 26.8, 26.9, 30.6, 32.5, 35.9 (CH_2, CHI), 92.1 (CHO).

Anal. Calcd for $C_8H_{15}IO_2$: C, 35.57; H, 5.60; I, 46.98. Found: C, 35.82; H, 5.65; I, 46.52.

2-{[1-(Iodomethyl)pentyl]peroxy}tetrahydro-2*H*-pyran (19)
Slightly yellow oil; R_f = 0.45 (TLC, hexane–EtOAc, 10:1).

^{1}H NMR (200.13 MHz, $CDCl_3$): δ = 0.79–0.95 (m, 3 H, CH_3), 1.14–1.79 (m, 12 H, CH_2), 3.26–4.03 (m, 4 H, CH_2O, CH_2I, CHO), 5.10–5.18 (m, 1 H, OCHO).

^{13}C NMR (50.32 MHz, $CDCl_3$): δ = 9.3, 8.3 (CH_2I), 13.7, 13.8 (CH_3CH_2), 19.68, 19.74, 22.0, 22.4, 25.0, 26.1, 27.3, 27.5, 27.7, 27.8, 31.7, 31.9 (CH_2), 62.5, 62.6 (CH_2O), 82.6, 82.7 (CHO), 100.5, 101.7 (OCHO).

Anal. Calcd for $C_{11}H_{21}IO_3$: C, 40.26; H, 6.45; I, 38.67. Found: C, 40.32; H, 6.28; I, 38.91.

2-[(2-Iodocyclopentyl)peroxy]tetrahydro-2*H*-pyran (20)
Slightly yellow oil; R_f = 0.25 (TLC, hexane–Et_2O, 20:1).

^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 1.45–2.30 (m, 12 H, CH_2), 3.53–3.65 (m, 1 H, CH_2O), 3.90–4.03 (m, 1 H, CH_2O), 4.58–4.66, 4.89–5.03 (m, 2 H, CHI, CHO), 5.05–5.14 (m, 1 H, OCHO).

^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 19.4, 19.8, 22.6, 25.0, 25.1, 27.6, 27.8, 27.9, 30.9, 31.3, 35.8 (CH_2, CI), 62.3, 62.8 (CH_2O), 92.7, 93.6 (CHO), 100.4, 101.4 (OCHO).

Anal. Calcd for $C_{10}H_{17}IO_3$: C, 38.48; H, 5.49; I, 40.66. Found: C, 38.70; H, 5.68; I, 40.82.

2-[(2-Iodocyclohexyl)peroxy]tetrahydro-2*H*-pyran (21)
Slightly yellow oil; R_f = 0.28 (TLC, hexane–Et_2O, 20:1).

^{1}H NMR (250.13 MHz, $CDCl_3$): δ = 1.18–2.37 (m, 14 H, CH_2), 3.54–3.67 (m, 1 H, CH_2O), 3.92–4.04 (m, 1 H, CH_2O), 4.10–4.22, 4.32–4.45 (m, 2 H, CHI, CHO), 5.16–5.21 (m, 1 H, OCHO).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 19.7, 19.9, 22.5, 22.6, 25.0, 25.1, 25.3, 25.4, 27.9, 28.6, 28.7, 30.67, 30.73, 35.5 (CH_2, CI), 62.6, 62.8 (CH_2O), 85.2, 85.4 (CHO), 101.0, 101.4 (OCHO).

2-[(2-Iodocyclooctyl)peroxy]tetrahydro-2*H*-pyran (22)
Slightly yellow oil; R_f = 0.32 (TLC, hexane–Et_2O, 20:1).

^{1}H NMR (200.13 MHz, $CDCl_3$): δ = 1.14–2.29 (m, 18 H, CH_2), 3.54–4.44 (m, 4 H, CH_2O, CHI, CHO), 5.20–5.29 (m, 1 H, OCHO).

^{13}C NMR (50.32 MHz, $CDCl_3$): δ = 19.81, 19.87, 25.0, 25.1, 25.5, 25.6, 27.0, 27.1, 27.8, 28.0, 29.3, 29.6, 30.9, 31.0, 32.0, 32.2, 35.8, 35.9 (CH_2), 62.6, 62.8 (CH_2O), 91.0, 91.5 (CHO), 100.4, 101.6 (OCHO).

Anal. Calcd for $C_{13}H_{23}IO_3$: C, 44.08; H, 6.54; I, 35.83. Found: C, 44.37; H, 6.31; I, 35.97.

1-*tert*-Butylperoxy-2-iodoalkanes 8 and 13 from Diiodoalkanes 30 and 31
A 50% *t*-BuOOH solution (3.6 g, 20 mmol; 4 mol per mole of diiodoalkane) in Et_2O, I_2 (0.13 or 0.64 g; 0.5 or 2.5 mmol; 0.1 or 0.5 mol per mole of diiodoalkane), and 1,2-diiodoalkane (5 mmol) were successively added to Et_2O (5 mL). The mixture was allowed to stand at 20–25 °C for 2 h. The isolation was performed analogously to the preparation of **8**–**14**.

The reactions of *tert*-butyl hydroperoxide with iodocyclohexane, 2-iodocyclohexanol, and 1,2-dibromocyclohexane were carried out analogously using I_2 in an amount of 0.5 mol per mole of halide.

Determination of the Competitive Influence of *t*-BuOOH and H_2O on Iodoperoxidation of Cyclohexene
A 50% *t*-BuOOH solution (5.27 g, 29.3 mmol, 8 mol per mole of cyclohexene) in Et_2O, H_2O (0.13 g, 7.32 mmol, 2 mol per mole of cyclohexene), I_2 (0.65 g, 2.56 mmol, 0.7 mol per mole of cyclohexene), and cyclohexene (0.3 g, 3.66 mmol) were successively added to Et_2O (10 mL). The mixture was allowed to stand at 20–25 °C for 5 h. Iodoperoxide **13** and iodoalkanol **28** were isolated analogously to **8**–**14**.

Acknowledgment

This work is supported by the Program for Support of Leading Scientific Schools of the Russian Federation (Grant NSh 5022.2006.3), the Grant of President of Russian Federation (No. MK-3515.2007.3) and the Russian Science Support Foundation.

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