

## Oxidative nucleophilic substitution reaction of alkyl iodides upon treatment with perchlorate and dinitramide anions. Synthesis of alkyl-substituted perchlorates

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Reactions of oxidative nucleophilic substitution of alkyl iodides with lithium perchlorate and dinitramide were studied. The reactions of alkyl iodides and lithium perchlorate, proceeding in the presence of nitronium tetrafluoroborate as an oxidant, furnished a series of new alkyl perchlorates, including those containing an adamantyl fragment. Spectral properties of alkyl perchlorates were studied in detail for the first time. The reactions of oxidative nucleophilic substitution of iodoacetic ester and lithium dinitramide, proceeding upon treatment with nitronium tetrafluoroborate or ozone, resulted in the substitution of an iodine atom with the nitrate anion.

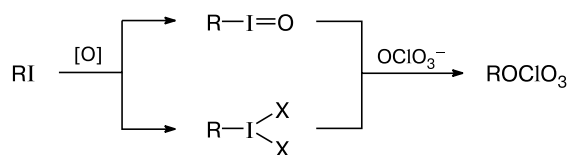
**Key words:** alkyl perchlorates, oxidative nucleophilic substitution, hypervalent iodine compounds, dinitramides.

A promising direction in the use of hypervalent iodine compounds<sup>1–3</sup> in organic synthesis is the reactions of oxidative nucleophilic substitution of iodine in alkyl iodides, in which the first step gives hypervalent compounds of tervalent iodine such as RI=O, RIX<sub>2</sub> (X = Cl, Br) capable of being involved in the S<sub>N</sub>2-type reactions<sup>4</sup> with various nucleophiles with the formation of the products of formal substitution of iodine atom with a functional group (Scheme 1).<sup>5–8</sup> These reactions are used for the substitution of an iodine atom in alkyl iodides with such weak nucleophiles as triflate, perchlorate, fluorosulfonate, tosylate anions.<sup>8,9</sup> Alkyl perchlorates obtained using such an approach are high-energy compounds, as well as they can be used as synthetic precursors of other classes of organic compounds, since a perchlorate group can be easily substituted with different nucleophiles.<sup>10</sup>

It is very interesting to study such a weak nucleophile as dinitramide anion<sup>11–13</sup> in the oxidative nucleophilic substitution reaction, for which only separate examples of nucleophilic substitution reactions are known.<sup>13</sup>

In the present work, we studied the reactions of nucleophilic substitution of an iodine atom with the perchlorate group proceeding in the presence of an oxidant for

Scheme 1

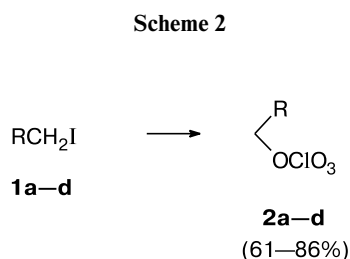


X = Cl, Br

a series of primary alkyl iodides **1a–e** (Schemes 2 and 3), including those containing an adamantyl and alkoxy-carbonyl substituents, as well as investigated a possibility of the use of dinitramide anion as a nucleophilic agent in the reaction with iodides.

Anhydrous lithium perchlorate well soluble in many organic solvents was used in the reactions with iodides **1a–e**, nitronium tetrafluoroborate was chosen as an oxidant, since it possesses a high reactivity, and its anion cannot compete with the perchlorate anion in the nucleophilic substitution reaction (see Schemes 2 and 3). The use in the reaction of a five-fold amount of LiClO<sub>4</sub> and a 2.5-fold excess of NO<sub>2</sub>BF<sub>4</sub> leads to a complete conversion

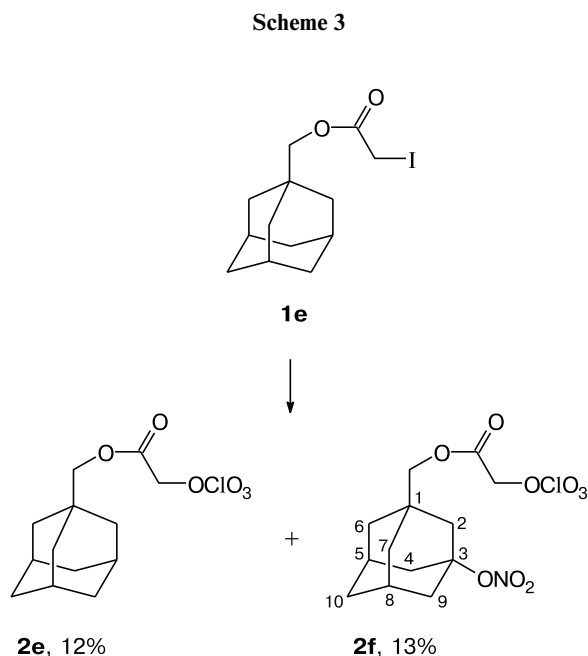
of iodides **1a–d** to the corresponding perchlorates **2a–d**, which were isolated by preparative column chromatography in high yields (see Scheme 2).



R = C<sub>7</sub>H<sub>15</sub> (**a**), C<sub>9</sub>H<sub>19</sub> (**b**), CO<sub>2</sub>Et (**c**), 1-Ad (**d**)

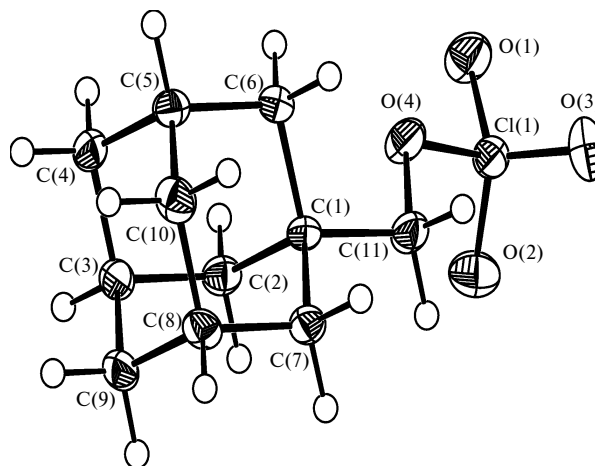
**Reagents:** LiClO<sub>4</sub> (5 equiv.), NO<sub>2</sub>BF<sub>4</sub> (2.5 equiv.)

It turned out that the reaction of (1-adamantyl)methyl iodoacetate (**1e**) with LiClO<sub>4</sub> in the presence of NO<sub>2</sub>BF<sub>4</sub> gave, together with perchlorate **2e**, the product of the substitution of a proton at the tertiary carbon atom of compound **2e** with the ONO<sub>2</sub> group, *i.e.*, (3-nitrato-1-adamantyl)methyl perchloroxyacetate (**2f**) (Scheme 3). According to the <sup>1</sup>H NMR spectroscopy data, the ratio of perchlorates **2e** and **2f** in the reaction mixture was 5 : 1, however, during chromatographic separation of the mixture, a significant amount of perchlorate **2e** decomposes on silica gel, which leads to a decrease in its content in the mixture of perchlorates, and the yields of the individual compounds **2e** and **2f** are 12 and 13%, respectively.



**Reagents:** LiClO<sub>4</sub> (5 equiv.), NO<sub>2</sub>BF<sub>4</sub> (2.5 equiv.), CH<sub>2</sub>Cl<sub>2</sub>.

The <sup>1</sup>H NMR spectra of perchlorates **2a–f** exhibit a downfield shift of the signals for the protons of the methylene fragments bonded to the OClO<sub>3</sub> group by



**Fig. 1.** Atom numbering scheme in the structure of perchlorate **2d**. Ellipsoids of displacements are given with 30% probability.

**Table 1.** Crystallographic characteristics of perchlorate **2d** and main parameters of the structure refinement

Parameter	Value
Molecular formula	C <sub>11</sub> H <sub>17</sub> ClO <sub>4</sub>
Molecular weight	248.70
<i>T</i> /K	120(2)
$\lambda$ /Å	0.71073
Crystal system	Triclinic
Space group	<i>P</i> $\bar{1}$
<i>a</i> /Å	6.8433(12)
<i>b</i> /Å	7.8108(14)
<i>c</i> /Å	11.306(2)
$\alpha$ /deg	74.585(3)
$\beta$ /deg	81.360(3)
$\gamma$ /deg	89.498(3)
<i>V</i> /Å <sup>3</sup>	575.69(18)
<i>Z</i>	2
$\rho_{\text{calc}}$ /g cm <sup>-3</sup>	1.435
$\mu$ /mm <sup>-1</sup>	0.328
<i>F</i> (000)	264
Crystal size/mm	0.30×0.10×0.10
$\theta$ range of data collection/deg	1.89–30.00
Range of indices <i>hkl</i>	–9 ≤ <i>h</i> ≤ 9, –10 ≤ <i>k</i> ≤ 10, –15 ≤ <i>l</i> ≤ 15
Independent reflections ( <i>R</i> <sub>int</sub> )	3338 (0.0385)
Number of parameters	145
GOOF ( <i>F</i> <sup>2</sup> )	1.004
<i>R</i> <sub>1</sub> / <i>wR</i> <sub>2</sub> ( <i>I</i> > 2 $\sigma$ ( <i>I</i> ))	0.0437/0.1050
<i>R</i> <sub>1</sub> / <i>wR</i> <sub>2</sub> (all reflections)	0.0757 / 0.1133
( $\Delta\rho_{\text{max}}/\Delta\rho_{\text{min}}$ )/e Å <sup>-3</sup>	0.411 / –0.343
Deposit number	CCDC 1058785

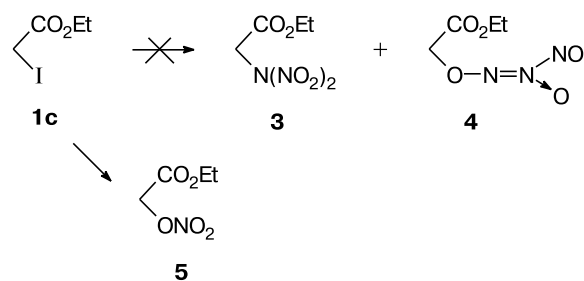
**Table 2.** Selected interatomic distances (*d*) in the structure of perchlorate **2d**

Bond	<i>d</i> /Å	Bond	<i>d</i> /Å
Cl(1)—O(1)	1.4085(14)	Cl(1)—O(2)	1.4111(14)
Cl(1)—O(3)	1.4118(14)	Cl(1)—O(4)	1.6029(13)
O(4)—C(11)	1.484(2)	C(1)—C(11)	1.521(2)
C(1)—C(6)	1.541(2)	C(1)—C(2)	1.544(2)
C(1)—C(7)	1.545(2)	C(2)—C(3)	1.538(2)
C(3)—C(4)	1.536(2)	C(3)—C(9)	1.537(2)
C(4)—C(5)	1.535(3)	C(5)—C(6)	1.539(2)
C(5)—C(10)	1.539(2)	C(7)—C(8)	1.538(2)
C(8)—C(9)	1.531(3)	C(8)—C(10)	1.535(2)

$\Delta\delta_{\text{H}}$  1.32±0.05 ppm as compared to the signals for the corresponding protons in the starting iodides **1a–e**. In the  $^{13}\text{C}$  NMR spectra of compounds **2a–f**, the signals for the carbon atoms of the  $\text{CH}_2\text{OCIO}_3$  group are found in the range  $\delta_{\text{C}}$  69.1–84.4. For perchlorates **2d,e**, four multiplets in the proton spectra and four signals in the carbon spectra corresponding to the mono-substituted at position 1 adamantyl fragment are present in the high-field region of the NMR spectra. In the case of perchlorate **2f**, the  $^1\text{H}$  NMR spectrum exhibits four multiplets and one singlet in the region of  $\delta_{\text{H}}$  1.47–2.44, whereas in the  $^{13}\text{C}$  NMR spectrum six signals are present in the high-field region ( $\delta_{\text{C}}$  30.2–41.1), which correspond to six methylene, two methine, and one quaternary carbon atoms. A quaternary carbon atom of the adamantane fragment of perchlorate **2f** bonded to the nitrate group was found more downfield at  $\delta_{\text{C}}$  89.4. This set of signals in the NMR spectra is a firm evidence of the presence in the structure of compound **2f** of 1,3-disubstituted adamantane fragment. The composition of perchlorates **2e,f** was confirmed by high resolution mass spectrometry data. The structure of perchlorate **2d** was unambiguously confirmed by X-ray crystallography (Fig. 1, Tables 1–3).

We for the first time studied alkyl iodides in the oxidative nucleophilic substitution reactions involving lithium dinitramide (LiDNA), using different oxidants on a mod-

el iodoacetic ester **1c**. It was shown that in the absence of an oxidant, iodide **1c** treated with both the lithium and the ammonium dinitramide did not undergo nucleophilic substitution even with a large excess of reagents. It was found that in the presence of the oxidant  $\text{NO}_2\text{BF}_4$ , the reaction of compound **1c** with LiDNA taken in an excess relative to the oxidant an iodine atom was not substituted with the nucleophile either. When an excess of  $\text{NO}_2\text{BF}_4$  relative to LiDNA was used, the iodide **1c** was completely converted, however, nitrate **5** was obtained in high yield instead of the expected products of *N*- or *O*-alkylation of dinitramide anion (dinitramide **3** or nitro diazene *N*-oxide **4**) (Scheme 4).

**Scheme 4**

**Reagents:**  $\text{NO}_2\text{BF}_4$  (4 equiv.), LiDNA<sub>4</sub> (2 equiv.),  $\text{CH}_2\text{Cl}_2$ .

To find out a possible pathway of the formation of ester **5**, we studied the reaction of iodide **1c** with  $\text{NO}_2\text{BF}_4$  in the absence of LiDNA, which proceeded with the formation of a complex mixture of unidentified products, among which the  $^1\text{H}$  NMR data showed the presence of ester **5** in insignificant amounts. This fact is an evidence of the involvement of LiDNA in the formation of nitrate **5**. The most probable is the scheme including the formation of the intermediate trinitramine from LiDNA and  $\text{NO}_2\text{BF}_4$ . Earlier,<sup>14</sup> the formation of trinitramine was detected in the reactions of dinitramide salts and  $\text{NO}_2\text{BF}_4$ , in this case it was noted that trinitramine at temperature

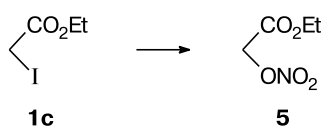
**Table 3.** Selected bond angles ( $\omega$ ) in the structure of perchlorate **2d**

Angle	$\omega$ /deg	Angle	$\omega$ /deg	Angle	$\omega$ /deg
O(1)—Cl(1)—O(2)	113.91(9)	C(6)—C(5)—C(10)	109.20(14)	C(6)—C(1)—C(7)	109.04(13)
O(2)—Cl(1)—O(3)	112.45(9)	C(8)—C(7)—C(1)	109.85(13)	C(3)—C(2)—C(1)	109.66(14)
O(2)—Cl(1)—O(4)	106.60(8)	C(9)—C(8)—C(7)	109.69(14)	C(4)—C(3)—C(2)	109.34(14)
C(11)—O(4)—Cl(1)	115.00(10)	C(8)—C(9)—C(3)	109.78(14)	C(5)—C(4)—C(3)	109.75(14)
C(11)—C(1)—C(2)	111.05(14)	O(4)—C(11)—C(1)	106.46(13)	C(4)—C(5)—C(10)	109.64(14)
C(11)—C(1)—C(7)	107.69(13)	O(1)—Cl(1)—O(3)	114.67(9)	C(5)—C(6)—C(1)	109.86(13)
C(2)—C(1)—C(7)	109.05(13)	O(1)—Cl(1)—O(4)	101.23(8)	C(9)—C(8)—C(10)	109.40(15)
C(4)—C(3)—C(9)	109.26(14)	O(3)—Cl(1)—O(4)	106.72(8)	C(10)—C(8)—C(7)	109.14(14)
C(9)—C(3)—C(2)	109.69(14)	C(11)—C(1)—C(6)	110.74(13)	C(8)—C(10)—C(5)	109.73(14)
C(4)—C(5)—C(6)	109.19(14)	C(6)—C(1)—C(2)	109.23(14)		

above  $-30\text{ }^{\circ}\text{C}$  is unstable and decomposes, in particular, with the formation of nitrate anions. Thus, trinitramine is the most probable source of nitrate anions in the reaction of iodoacetic ester **1c** with  $\text{NO}_2\text{BF}_4$  in the presence of lithium dinitramide salt.

It turned out that the reaction of iodoacetate **1c** with LiDNA in the presence of gaseous ozone as an oxidant also proceeded with the formation of nitrate **5** (Scheme 5). It is probable that in this case LiDNA undergoes oxidative destruction, which results in the formation of nitrate anion serving as a nucleophile in the reaction with the product of oxidation of ester **1c**. The use in the reaction of iodide **1c** with LiDNA of oxidants weaker than  $\text{NO}_2\text{BF}_4$  and ozone, such as phenyliodobis(trifluoroacetate), nitrozonium tetrafluoroborate, *m*-chloroperbenzoic acid, has proved inefficient, and the starting iodoacetic ester **1c** was recovered from the reaction mixture unchanged.

Scheme 5



**Reagents and conditions:**  $\text{O}_3$ , LiDNA (2 equiv.),  $\text{CH}_2\text{Cl}_2$ ,  $10\text{--}20\text{ }^{\circ}\text{C}$ .

In conclusion, the reactions of alkyl iodides with lithium perchlorate in the presence of  $\text{NO}_2\text{BF}_4$  furnished a series of new alkyl-substituted perchlorates, which are of interest to be studied in the nucleophilic substitution reactions involving weak nucleophiles.<sup>15</sup> It was found that the use of lithium dinitramide in the oxidative nucleophilic substitution reactions in alkyl iodides led to the generation of nitrate anions and the formation of alkyl nitrates.

### Experimental

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker Avance-400 spectrometer (400 and 100 MHz, respectively). The signals of chloroform ( $\delta_{\text{H}}$  7.24,  $\delta_{\text{C}}$  77.10) were used as an internal standard in the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra. Melting points were measured on a Electrothermal 9100 appliance. High resolution mass spectra (HRMS) were recorded on a JEOL GCMate II mass spectrometer (70 eV, ESI). Reaction progress and purity of chemical compounds were monitored by TLC (Silufol-UV-254). X-ray diffraction experiment was performed on a STADI VARI Pilatus-100 K diffractometer. Preparative column chromatography was performed on silica gel with particle size of  $0.04\text{--}0.06\text{ mm}$  (Macherey-Nagel GmbH&Co KG). Analytical thin-layer chromatography was carried out on silica gel (Silufol plates on aluminum support), visualization in iodine vapors or in aqueous solution of potassium permanganate. Ethyl acetate dried by distilla-

tion over calcium hydride, anhydrous lithium perchlorate was obtained by calcination of  $\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$  at  $240\text{ }^{\circ}\text{C}$ ; LiDNA was obtained by the reaction of ammonium dinitramide\* with an aqueous solution of LiOH.<sup>11</sup>

*Attention! Alkyl perchlorates are extremely unstable explosives. All the manipulations with these compounds should be carried out with observance of the corresponding safety precautions. The isolation of more than 10 mg of alkyl perchlorates in the individual state is very dangerous.*

**Synthesis of alkyl perchlorates (general procedure).** Anhydrous lithium perchlorate (532 mg, 5 mmol) was added to a solution of alkyl iodide (1 mmol in ethyl acetate (5 mL)\*\* at room temperature under an inert atmosphere. Then, nitronium tetrafluoroborate (333 mg, 2.5 mmol) was added to the suspension obtained with stirring at  $0\text{--}5\text{ }^{\circ}\text{C}$ . The reaction mixture was stirred at room temperature for 36 h, diluted with ice-cold water (10 mL), the aqueous layer was extracted with  $\text{CH}_2\text{Cl}_2$  ( $3 \times 5\text{ mL}$ ), the extract was washed with water ( $2 \times 5\text{ mL}$ ) and dried with  $\text{MgSO}_4$ . The solvent was evaporated at reduced pressure, the residue was dried *in vacuo* until the iodine color completely disappeared. The alkyl perchlorate was purified by preparative column chromatography.

***n*-Octyl perchlorate (2a).** The yield was 151 mg (71%). A colorless oil,  $R_f$  0.75 (hexane).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ),  $\delta$ : 0.90 (br.t, 3 H,  $\text{CH}_3$ ,  $^3J = 6.7\text{ Hz}$ ); 1.21–1.52 (m, 10 H); 1.76–1.90 (m, 2 H); 4.55 (t, 2 H,  $\text{OCH}_2$ ,  $^3J = 6.6\text{ Hz}$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ),  $\delta$ : 14.0 ( $\text{CH}_3$ ); 22.6 ( $\text{CH}_2$ ); 25.3 ( $\text{CH}_2$ ); 27.4 ( $\text{CH}_2$ ); 28.9 ( $\text{CH}_2$ ); 29.0 ( $\text{CH}_2$ ); 31.7 ( $\text{CH}_2$ ); 76.3 ( $\text{OCH}_2$ ).

***n*-Decyl perchlorate (2b).** The yield was 206 mg (86%). A colorless oil,  $R_f$  0.80 (hexane).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ),  $\delta$ : 0.90 (br.t, 3 H,  $\text{CH}_3$ ,  $^3J = 6.7\text{ Hz}$ ); 1.21–1.48 (m, 14 H); 1.76–1.86 (m, 2 H); 4.55 (t, 2 H,  $\text{OCH}_2$ ,  $^3J = 6.6\text{ Hz}$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ),  $\delta$ : 13.9 ( $\text{CH}_3$ ); 22.6 ( $\text{CH}_2$ ); 25.2 ( $\text{CH}_2$ ); 27.3 ( $\text{CH}_2$ ); 28.8 ( $\text{CH}_2$ ); 29.2 ( $\text{CH}_2$ ); 29.3 ( $\text{CH}_2$ ); 29.4 ( $\text{CH}_2$ ); 31.8 ( $\text{CH}_2$ ); 76.1 ( $\text{OCH}_2$ ).

**Ethyl 2-perchloryloxyacetate (2c).** The yield was 136 mg (74%). A colorless oil,  $R_f$  0.60 (hexane–ether, 2 : 1).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ),  $\delta$ : 1.30 (t, 3 H,  $\text{CH}_3$ ,  $^3J = 7.1\text{ Hz}$ ); 4.29 (q, 2 H,  $\text{CH}_2\text{CH}_3$ ,  $^3J = 7.1\text{ Hz}$ ); 4.95 (s, 2 H,  $\text{CH}_2\text{OCl}$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ),  $\delta$ : 13.9 ( $\text{CH}_3$ ); 62.6 ( $\text{CH}_2\text{CH}_3$ ); 69.1 ( $\text{CH}_2\text{OCl}$ ); 164.1 (C).

**(1-Adamantyl)methyl perchlorate (2d).** The yield was 151 mg (61%). White crystals, m.p.  $31\text{--}32\text{ }^{\circ}\text{C}$ ,  $R_f$  0.65 (hexane).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ),  $\delta$ : 1.57–1.64 (m, 6 H,  $\text{CH}_2$ , Ad); 1.65–1.73 (m, 3 H,  $\text{CH}_2$ , Ad); 1.73–1.82 (m, 3 H,  $\text{CH}_2$ , Ad); 2.02–2.08 (m, 3 H, CH, Ad); 4.11 (s, 2 H,  $\text{CH}_2\text{O}$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ),  $\delta$ : 27.75 (d, 3 CH, Ad,  $^2J_{\text{C,H}} = 133\text{ Hz}$ ); 36.6 (t, 3  $\text{CH}_2$ , Ad,  $^2J_{\text{C,H}} = 127\text{ Hz}$ ); 37.2 (s, Ad); 38.6 (t, 3  $\text{CH}_2$ , Ad,  $^2J_{\text{C,H}} = 128\text{ Hz}$ ); 84.4 (t,  $\text{CH}_2\text{O}$ ,  $^2J_{\text{C,H}} = 150\text{ Hz}$ ).

**(1-Adamantyl)methyl 2-perchloryloxyacetate (2e).** The yield was 37 mg (12%). A light yellow oil,  $R_f$  0.65 (hexane–ether, 2 : 1). Found:  $m/z$  329.0762 [ $\text{M} + \text{Na}$ ] $^+$ .  $\text{C}_{13}\text{H}_{19}\text{NaO}_6\text{Cl}$ . Calculated:  $M = 329.0768$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ),  $\delta$ : 1.51–1.60 (m, 6 H,  $\text{CH}_2$ , Ad); 1.62–1.70 (m, 3 H,  $\text{CH}_2$ , Ad); 1.70–1.79 (m, 3 H,  $\text{CH}_2$ , Ad); 1.97–2.05 (m, 3 H, CH, Ad); 3.86 (s, 2 H,  $\text{AdCH}_2\text{O}$ ); 5.01 (s, 2 H,  $\text{CH}_2\text{OCl}$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ),  $\delta$ : 27.9 (3 CH, Ad);

\* The authors are grateful to academicians of the RAS Yu. M. Mikhailov for providing with the samples of ammonium dinitramide.

\*\* In the case of iodides **1c** and **1e**, dichloromethane was used as a solvent.

33.3 (s, Ad); 36.8 (3 CH<sub>2</sub>, Ad); 39.0 (3 CH<sub>2</sub>, Ad); 69.0 (OCH<sub>2</sub>Ad); 75.8 (OCH<sub>2</sub>Cl); 164.3 (C=O).

**(1-Adamantyl-3-nitrato)methyl 2-perchloroxyacetate (2f).**

The yield was 48 mg (13%). A light yellow oil, *R*<sub>f</sub> 0.50 (hexane—ether, 2 : 1). Found: *m/z* 390.0551 [M + Na]<sup>+</sup>. C<sub>13</sub>H<sub>18</sub>NaO<sub>9</sub>Cl. Calculated: M = 390.0562. Found: *m/z* 406.0294 [M + K]<sup>+</sup>. C<sub>13</sub>H<sub>18</sub>KO<sub>9</sub>Cl. Calculated: M = 406.0302. <sup>1</sup>H NMR (CDCl<sub>3</sub>), δ: 1.47–1.61 (m, 4 H, C(4)H<sub>2</sub>, C(9)H<sub>2</sub>); 1.62–1.76 (m, 2 H, C(10)H<sub>2</sub>); 1.97 (s, 2 H, C(2)H<sub>2</sub>); 2.05–2.17 (m, 4 H, C(6)H<sub>2</sub>, C(7)H<sub>2</sub>); 2.34–2.44 (m, 2 H, C(5)H, C(8)H); 3.97 (s, 2 H, OCH<sub>2</sub>Ad); 5.03 (s, 2 H, CH<sub>2</sub>OCl). <sup>13</sup>C NMR (CDCl<sub>3</sub>), δ: 30.2 (C(5)H, C(8)H); 35.1 (C(9)H<sub>2</sub>); 37.4 (C(1)); 37.6 (C(4)H<sub>2</sub>, C(10)H<sub>2</sub>); 39.0 (C(6)H<sub>2</sub>, C(7)H<sub>2</sub>); 41.1 (C(2)H<sub>2</sub>); 68.9 (OCH<sub>2</sub>Ad); 74.0 (OCH<sub>2</sub>Cl); 89.4 (C(3)), 164.2 (C=O) (the signals in the NMR spectra of perchlorate **2f** were assigned using the gHSQC (through the direct spin-spin coupling constant C—H) and the gHMBC procedures (through the remote spin-spin coupling constants). Numbering of carbon atoms is given in Scheme 3).

**Reaction of iodide 1c with LiDNA in the presence of NO<sub>2</sub>BF<sub>4</sub>.**

The reagent LiDNA (226 mg, 2 mmol) was added to a solution of iodide **1c** (214 mg, 1 mmol) in dichloromethane (5 mL) at room temperature under an inert atmosphere. Then, nitronium tetrafluoroborate (532 mg, 4 mmol) was added to the suspension with stirring at 0–5 °C. The reaction mixture was stirred at room temperature for 24 h, diluted with ice-cold water (10 mL), the aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3×5 mL), the extract was washed with water (2×5 mL) and dried with MgSO<sub>4</sub>. The solvent was evaporated at reduced pressure, the residue was dried *in vacuo* until the iodine color completely disappeared. The nitrate **5** was purified by preparative column chromatography.

**Ethyl 2-nitratoacetate (5)** (According to the NMR spectral data, the sample of nitrato ester **5** obtained according to the procedure described above is identical with the sample of this compound obtained by us earlier<sup>16</sup> by the reaction of nitrogen pentoxide and ethyl (diazo)acetate). The yield was 100 mg (67%). A light yellow oil, *R*<sub>f</sub> 0.40 (hexane—ethyl acetate, 4 : 1). <sup>1</sup>H NMR (CDCl<sub>3</sub>), δ: 1.31 (t, 3 H, CH<sub>3</sub>, <sup>3</sup>*J* = 7.1 Hz); 4.30 (q, 2 H, CH<sub>2</sub>CH<sub>3</sub>, <sup>3</sup>*J* = 7.1 Hz); 4.92 (s, 2 H, CH<sub>2</sub>OCl). <sup>13</sup>C NMR (CDCl<sub>3</sub>), δ: 13.8 (CH<sub>3</sub>); 62.9 (CH<sub>2</sub>CH<sub>3</sub>); 67.2 (CH<sub>2</sub>O); 167.2 (C).

**Reaction of iodide 1c with LiDNA in the presence of ozone.**

An ozone—oxygen mixture (4–5 vol.% of ozone) was passed through a suspension of iodide **1c** (214 mg, 1 mmol), LiDNA (226 mg, 2 mmol), and dichloromethane (10 mL) at 10–20 °C for 15–20 min (until the iodine color completely disappeared). The reaction mixture was filtered, the solvent was evaporated at

reduced pressure, the product **5** was purified by preparative column chromatography to obtain nitrate **5** (80 mg, 54%).

## References

1. V. V. Zhdankin, P. J. Stang, *Chem. Rev.*, 2008, **108**, 5299.
2. V. V. Zhdankin, A. Y. Kuposov, B. C. Netzel, N. V. Yashin, B.P. Rempel, M. J. Ferguson, R. R. Tykwinski, *Angew. Chem.*, 2003, **42**, 2194.
3. V. V. Zhdankin, A. Y. Kuposov, N. V. Yashin, *Tetrahedron Lett.*, 2002, **43**, 5735.
4. N. S. Zefirov, V. V. Zhdankin, A. S. Koz'min, *Tetrahedron Lett.*, 1986, **27**, 1845.
5. N. S. Zefirov, V. V. Zhdankin, A. S. Koz'min, *Izv. Akad. Nauk, Ser. Khim.*, 1982, 1676 [*Bull. Acad. Sci. USSR, Div. Chem. Sci. (Engl. Transl.)*, 1982, **31**].
6. R. I. Davidson, P. J. Kropp, *J. Am. Chem. Soc.*, 1982, **47**, 1904.
7. P. H. McCabe, C. I. de Jenga, A. Stewart, *Tetrahedron*, 1981, **22**, 3679.
8. N. S. Zefirov, V. V. Zhdankin, A. S. Koz'min, *Russ. Chem. Rev.*, 1988, **57**, 1815.
9. N. S. Zefirov, V. V. Zhdankin, G. V. Makhon'kova, Yu. V. Dan'kov, A. S. Koz'min, *J. Org. Chem.*, 1985, **50**, 1872.
10. N. S. Zefirov, V. V. Zhdankin, A. S. Koz'min, *Dokl. Akad. Nauk SSSR*, 1982, **262**, 104 [*Dokl. Chem. (Engl. Transl.)*, 1982].
11. O. A. Luk'yanov, O. V. Anikin, V. P. Gorelik, V. A. Tartakovsky, *Russ. Chem. Bull. (Engl. Transl.)*, 1994, **43**, 1457 [*Izv. Akad. Nauk, Ser. Khim.*, 1994, 1546].
12. O. A. Luk'yanov, V. A. Tartakovsky, *Ros. Khim. Zh. [Russ. Chem. J.]*, 1997, **41**, 5.
13. O. A. Luk'yanov, N. I. Shlykova, V. A. Tartakovsky, *Russ. Chem. Bull. (Engl. Transl.)*, 1994, **43**, 1680 [*Izv. Akad. Nauk, Ser. Khim.*, 1994, 1775].
14. M. Rahm, S. V. Dvinskikh, I. Furo, T. Brinck, *Angew. Chem., Int. Ed.*, 2011, **50**, 1145.
15. N. S. Zefirov, A. S. Koz'min, *Acc. Chem. Res.*, 1985, **18**, 154.
16. O. A. Ivanova, N. V. Yashin, E. B. Averina, Yu. K. Grishin, T. S. Kuznetsova, N. S. Zefirov, *Russ. Chem. Bull. (Int. Ed.)*, 2001, **50**, 2101 [*Izv. Akad. Nauk, Ser. Khim.*, 2001, 2008].

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