Chlorination of Oximes with Aqueous H_2O_2/HCl System: Facile Synthesis of *gem*-Chloronitroso- and *gem*-Chloronitroalkanes, *gem*-Chloronitroso- and *gem*-Chloronitrocycloalkanes

Alexander O. Terent'ev,* Igor B. Krylov, Yuri N. Ogibin, Gennady I. Nikishin

N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 47 Leninsky prosp., 119991 Moscow, Russia
Fax +7(495)1355328; E-mail: terentev@ioc.ac.ru

Received 5 June 2006

Abstract: Chlorination of cyclic and linear ketone oximes with aqueous H_2O_2/HCl in a two-phase dichloromethane–water system selectively affords *gem*-chloronitroso compounds in yields of up to 94%. One-pot oxidation of the resulting *gem*-chloronitroso compounds with peracetic acid, prepared in situ, gives *gem*-chloronitroalkanes and cycloalkanes in yields of up to 82%. The advantages of the method are that it is facile and environmentally benign and does not require gaseous chlorine.

Key words: oximes, *gem*-chloronitroso compounds, *gem*-chloronitro compounds, chlorination, oxidation, hydrogen peroxide

Halogenation of organic compounds with an H_2O_2/HHal system has received wide acceptance in the last decades.[1–16] This system is most extensively used for halogenation of arenes,[1–3,7–14,16] alkenes,[1,6] and ketones.[4,5,15] The diversity of halogenation and oxidation processes as a result of generation of several active molecules (HHalO, H_2HalO^+, and Hal_2) in the H_2O_2/HHal system[17–19] allows the pathway and selectivity of the reactions to be varied over a wide range. The aqueous H_2O_2/HCl chlorination system is as inexpensive as molecular chlorine and preferable from the viewpoint of safety. In the present study, a new way of using the H_2O_2/HCl system for halogenation of organic compounds is reported and exemplified by the synthesis of *gem*-chloronitroso- and chloronitrohydrocarbons from oximes.

These compounds are of considerable interest as intermediates in organic synthesis. *gem*-Chloronitrosoalkanes and cycloalkanes have found use in the synthesis of *gem*-chloronitro compounds,[20,21] dihalides,[22,23] oxazines,[24–36] and O-allylated oximes.[37] *gem*-Chloronitroalkanes and cycloalkanes are used in the synthesis of nitro compounds,[20,38,39] esters of α,β-unsaturated acids,[40–42] and α-nitroalkylphosphonates.[43]

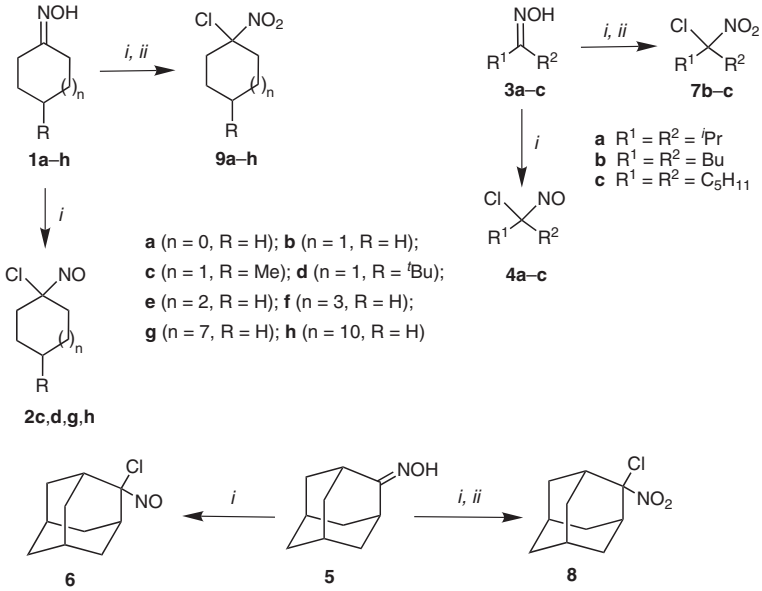
Procedures for the synthesis of *gem*-chloronitroso compounds are based on chlorination of oximes with chlorine,[21,22,44–47] *tert*-butyl hypochlorite,[36] and *N*-*tert*-butyl *N*-chlorocyanamide.[48] Since low-molecular-weight *gem*-chloronitroso compounds are unstable, syntheses with the use of these compounds are generally performed without their isolation. *gem*-Chloronitro compounds are synthesized primarily from oximes by chlorination followed by oxidation with an ozone-oxygen mixture,[49] oxone,[50] chlorotriazines,[51] or chloroperoxidases.[52] The preparation of *gem*-chloronitro compounds in low yields by the reactions of oximes with the H_2O_2/HCl synthesis was documented.[53] *gem*-Chloronitro compounds can also be synthesized by the reactions of nitro compounds with CCl_4,[54] by reductive dehalogenation of *gem*-bromonitro compounds followed by the reaction with NCS,[55] by chlorination of salts of nitro compounds,[21] or by oxidation of *gem*-chloronitroso compounds with a tetrabutylammonium hydrosulfate/aqueous sodium hypochlorite system[20] or atmospheric oxygen under irradiation.[47]

In the present study, the synthesis of *gem*-chloronitroso compounds was carried out in the two-phase aqueous H_2O_2/HCl/CH_2Cl_2 system. An aqueous 34% HCl solution was added to a solution of oxime **1**, **3**, or **5** in CH_2Cl_2, the reaction mixture was warmed to 38–40 °C, and aqueous 37% H_2O_2 was added. The resulting two-phase system contained a bright blue lower layer. Treatment of the latter afforded *gem*-chloronitroso compounds (Scheme 1).

We chose cyclododecanone oxime (**1g**) as a model compound to examine the influence of the reaction conditions on the synthesis of chloronitroso compounds. The chlorination product of **1g**, *viz*. 1-chloro-1-nitrosocyclododecane (**2g**), is a stable and convenient compound. The results of chlorination of oxime **1g** and oximes **1c**, **1d**, **1h**, **3a**–**c**, and **5** are summarized in Table 1.

The nature of the solvent and the phase composition of the system are the key factors determining the yield of nitroso compound **2g**. The reactions were carried out with the use of MeOH, THF, dioxane, AcOH (homogeneous systems, runs 4–7), benzene, and CH_2Cl_2 (heterogeneous systems, runs 1–3). After examination of different reaction conditions for chlorination of oxime **1g**, we succeeded in preparing product **2g** in high yield (85–94%) only with the use of a heterogeneous system (runs 1–3). An increase in the molar excess of H_2O_2 from 2.5 to 4 (runs 1 and 2, respectively) leads to a slight decrease in the yield of **2g** due to the formation of a small amount of chloronitro compound **9g**. The yields of **2g** are no more than 77% by chlorination of oxime **1g** in a homogeneous system (runs 4–7). Presumably, different results of chlorination are attributed to the fact that the reaction in heterogeneous systems (Scheme 2) occurs in an organic solvent under the action of molecular chlorine (Table 1, runs 1–3 and 8–14),

SYNTHESIS 2006, No. 22, pp 3819–3824
Advanced online publication: 09.10.2006
DOI: 10.1055/s-2006-950304; Art ID: P06706SS



Scheme 1 *Reagents and conditions*: *i*. aq H_2O_2/HCl/CH_2Cl_2, 20 min, 38–40 °C; *ii*. aq H_2O_2–AcOH, 2–12 h, 25–30 °C.

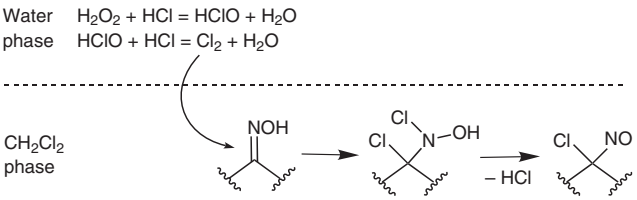
Table 1 Chlorination of Oximes **1c**, **1d**, **1h**, **1g**, **3a–c**, and **5** with the Aqueous H_2O_2/HCl System[a]

Run	Oxime	Solvent	H_2O_2/oxime molar ratio	Product	Yield (%)[b]
1	**1g**	CH_2Cl_2	2.5	**2g**	94
2	**1g**	CH_2Cl_2	4	**2g**	85
3	**1g**	benzene	2.5	**2g**	84
4[c]	**1g**	MeOH	2.5	**2g**	trace
5[c]	**1g**	THF	2.5	**2g**	73
6[c]	**1g**	dioxane	3	**2g**	77
7[c]	**1g**	AcOH	3	**2g**	32
8	**1c**	CH_2Cl_2	2.5	**2c**	79
9	**1d**	CH_2Cl_2	2.5	**2d**	84
10	**1h**	CH_2Cl_2	2.5	**2h**	89
11	**3a**	CH_2Cl_2	2.5	**4a**	78
12	**3b**	CH_2Cl_2	2.5	**4b**	87
13	**3c**	CH_2Cl_2	2.5	**4c**	88
14	**5**	CH_2Cl_2	2.1	**6**	76

[a] For general reaction conditions, see experimental.
[b] The yields are given with respect to the isolated product.
[c] The reaction mixture was warmed at 45–50 °C.

whereas deoximation of oximes followed by chlorination of the resulting ketones are the essential side processes in homogeneous systems (runs 4–7).

In heterogeneous conditions with the use of CH_2Cl_2 as the solvent, products **2c**,**d**,**h**, **4a–c**, and **6** were obtained in 76–89% yields (runs 8–14). Compound **6** was synthesized in the presence of a smaller excess of H_2O_2 (run 14) because the nitroso group in this compound is more prone to further oxidation.



Scheme 2

Under the condition optimized for chlorination of cyclododecanone oxime **1g**, we performed chlorination of oximes **1a**,**b**,**e** containing five-to-seven-membered rings. It was difficult to directly estimate the yield of chloronitroso compounds because of their lability. The fact that oxidation of these oximes affords chloronitroso compounds in high yields is indirectly evident from the yields of chloronitro compounds **9a**,**b**,**e** because the one-pot synthesis of the latter proceeds through the formation of chloronitroso compounds.

As mentioned above, a simple increase in the excess of hydrogen peroxide in run 2 (Table 1) did not lead to the formation of chloronitrocyclododecane (**2g**) from oxime with good selectivity. With the aim of developing a convenient procedure for the synthesis of chloronitro compounds **7a–c**, **8**, and **9a–h**, we examined oxidation of oximes with peracetic acid prepared in situ (Scheme 1, Table 2). The course of the reaction was monitored visually by observing the decrease in the intensity of the blue color of the reaction mixture. After completion of the reactions, the solutions turned almost colorless.

According to this procedure, oxidative chlorination of oximes was carried out in two steps. Initially, the reaction with a fourfold molar excess of hydrogen peroxide afford-

Table 2 Synthesis of *gem*-Chloronitroalkanes and *gem*-Chloronitrocycloalkanes[a]

Run	15	16	17	18	19	20	21	22	23	24	25	26	27
Oxime	**3a**	**3b**	**3c**	**5**	**1a**	**1b**	**1b**	**1c**	**1d**	**1e**	**1f**	**1g**	**1h**
Yield (%) of chloronitro compounds[b]	**7a** –[c]	**7b** 81	**7c** 82	**8** 82	**9a** 74	**9b** 79	**9b** 63[d]	**9c** 67	**9d** 73	**9e** 60	**9f** 48	**9g**[e] 81	**9h** 80

[a] For general reaction conditions, see experimental.
[b] The yields are given with respect to the isolated product.
[c] Compound **7a** was not obtained.
[d] The HCO_2H/H_2O_2 system was used as an oxidizing agent for the chloronitroso compound formed in situ.
[e] The synthesis was scaled with increasing amounts of the reagents by a factor of 10.

ed predominantly chloronitroso compounds and small amounts of chloronitro compounds. Then acetic acid and a tenfold excess of hydrogen peroxide were added to the bright blue reaction mixture and the mixture was stirred until it turned colorless.

Attempts to synthesize *gem*-chloronitro compound **7a** from diisopropylketone oxime **3a** containing the sterically hindered reaction center essentially failed (run 15). Chloronitro compounds **9e** (run 24) and **9f** (run 25) were prepared in moderate yields (60% and 48%, respectively). Apparently, this is attributed to low stability of intermediate chloronitroso compounds, which have no time to be oxidized to nitro compounds and are consumed in competitive side reactions. The yields of nitro compounds in runs 16–23 and 26–27 are rather high (74–82%). The synthesis of 1-chloro-1-nitrocyclohexane (**9b**) demonstrated that the reaction with performic acid prepared in situ affords the target product in lower yield (63%, run 21) than the reaction with peracetic acid (79%, run 20).

Nitroso and nitro compounds have low polarity and are readily soluble in hexane in petroleum ether, due to which these solvents are convenient both for isolation from the reaction mixture and chromatography.

In conclusion, we found the conditions for the synthesis of *gem*-chloronitrosoalkanes and chloronitrosocycloalkanes by oxidation of linear alkanone and cycloalkanone oximes with aqueous H_2O/HCl. The two-phase dichloromethane–water system is a mixture of choice for this purpose. The one-pot synthesis of *gem*-chloronitroalkanes and chloronitrocycloalkanes was carried out by oxidation of the corresponding nitroso compounds with peracetic acid prepared in situ. Depending on the structure of oximes, chloronitro and chloronitroso compounds were synthesized in 48–94% yields. The method is facile and environmentally benign and affords the target products in high yields.

The NMR spectra were recorded on Bruker DRX-500 (125 MHz for ^{13}C), Bruker WM-250 (250.13 MHz for ^1H and 62.9 MHz for ^{13}C), and Bruker AC-200 (200.13 MHz for ^1H and 50.32 MHz for ^{13}C) spectrometers in $CDCl_3$. The TLC analysis was carried out on chromatographic Silufol UV-254 plates. Column chromatography was performed with the use of 63–200 mesh silica gel (Merck). Melting points were determined on a Kofler hot stage and are uncorrected. Ketones, hydroxylamine hydrochloride, and cyclohexanone oxime (**1b**) were commercial reagents (Aldrich and Acros). An aq 37% H_2O_2 solution and an aq 34% HCl solution of high purity grade were used without additional purification.

Oximes **1a**–**h**, **3a**–**c**, and **5** were prepared by the reaction of $NH_2OH{\cdot}HCl$ with the corresponding ketones.

1a, mp 56–57.5 °C (Lit.[56] mp 57–58.5 °C); **1c**, mp 35–37 °C (Lit.[57] mp 36–37 °C); **1d**, mp 86–88 °C (Lit.[58] mp 87–89 °C); **1e**, bp 70–73 °C/1 Torr (Lit.[59] bp 150–152 °C/20 Torr); **1f**, mp 35–37 °C (Lit.[59] mp 35–37 °C); **1g**, mp 133–135 °C (Lit.[60] mp 133–134 °C); **1h**, mp 76–78 °C (Lit.[59] mp 76–77 °C); **3a**, mp 31–33 °C (Lit.[61] mp 34 °C); **3b**, bp 110–112 °C/8 Torr) (Lit.[62] bp 125 °C/15 Torr); **3c**, bp 132–134 °C/8 Torr) (Lit.[63] bp 144.2 °C/12 Torr); **5**, mp 163–164.5 °C (Lit.[64] mp 164.5–165.5 °C).

The solvents CH_2Cl_2, MeOH, benzene, THF, dioxane, AcOH, HCO_2H, and petroleum ether (40–70) of high purity grade were used without additional purification.

Chloronitroso Compounds; General Procedure

Oxime (0.5 g, 2.09–3.94 mmol) was dissolved in CH_2Cl_2 (MeOH, benzene, THF, dioxane, or AcOH; 10 mL), a five-fold molar excess of aq 34% HCl (1.125–2.11 g, 10.45–19.63 mmol) was added, and the mixture was warmed to 38–40 °C (45–50 °C for MeOH, THF, dioxane, or AcOH). Then aq 37% H_2O_2 solution (2.1–4-fold molar excess) was added with stirring in 1 min. The mixture was stirred for 20 min and cooled to 20 °C. Petroleum ether (50 mL) and H_2O (50 mL) were added. The lower layer was separated, and the upper layer was washed with H_2O (4 × 10 mL), dried ($MgSO_4$), filtered and concentrated. The target chloronitroso compounds were isolated by flash chromatography using petroleum ether as the eluent.

1-Chloro-4-methyl-1-nitrosocyclohexane (2c)[65]

Blue oil; mixture of isomers; R_f = 0.59 (petroleum ether).

^1H NMR (250.13 MHz, $CDCl_3$): δ = 0.91–1.10 (m, 3 H, CH_3), 1.35–1.93 (m, 7 H, CH, CH_2), 2.49–2.77 (m, 2 H, CH_2).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 20.4, 21.8 (CH_3), 29.7, 30.9, 31.4, 32.0, 32.8, 34.3 (CH, CH_2), 111.9, 118.8 (C).

4-*tert*-Butyl-1-chloro-1-nitrosocyclohexane (2d)[20]

Blue oil; mixture of isomers; R_f = 0.61 (petroleum ether).

^1H NMR (250.13 MHz, $CDCl_3$): δ = 0.87, 0.94 (s, 9 H, *t*-C_4H_9), 1.26–2.09 (m, 7 H, CH, CH_2), 2.48–2.82 (m, 2 H, CH_2).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 22.4, 25.2, 27.4 (for both isomers), 31.8, 32.4 (C), 33.3, 37.3 (CH_2), 46.7, 46.8 (CH), 119.2, 109.5 (CCl).

1-Chloro-1-nitrosocyclododecane (2g)[21]

Blue crystals; mp 55.5–56.5 °C ($CHCl_3$) (Lit.[21] mp 53–55 °C); R_f = 0.57 (petroleum ether).

^1H NMR (200.13 MHz, $CDCl_3$): δ = 1.30–1.92 (m, 20 H, CH_2), 2.29–2.52 (m, 2 H, CH_2C).

^{13}C NMR (50.32 MHz, $CDCl_3$): δ = 20.2, 22.1, 22.6, 25.6, 26.2 (CH_2), 32.6 (CH_2C), 118.8 (C).

Anal. Calcd for $C_{12}H_{22}ClNO$: C, 62.19; H, 9.57; N, 6.04. Found: C, 62.28; H, 9.53; N, 6.08.

1-Chloro-1-nitrosocyclopentadecane (2h)[66]
Blue oil; R_f = 0.63 (petroleum ether).

^{1}H NMR (250.13 MHz, $CDCl_3$): δ = 1.25–1.70 (m, 24 H, CH_2), 1.79–1.94 (m, 2 H, CH_2C), 2.30–2.45 (m, 2 H, CH_2C).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 22.4 26.4, 26.6, 26.7, 27.0, 27.5 (CH_2), 35.4 (CH_2C), 118.5 (C).

Anal. Calcd for $C_{15}H_{28}ClNO$: C, 65.79; H, 10.31; N, 5.11; Cl, 12.95. Found: C, 65.84; H, 10.67; N, 5.22; Cl, 12.89.

3-Chloro-2,4-dimethyl-3-nitrosopentane (4a)
Blue oil; R_f = 0.6 (petroleum ether).

^{1}H NMR (250.13 MHz, $CDCl_3$): δ = 0.88 (d, J = 6.6 Hz, 6 H, CH_3), 1.05 (d, J = 6.6 Hz, 6 H, CH_3), 3.33 (m, 2 H, CH).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 16.7, 17.3 (CH_2), 34.3 (CH_2C), 120.7 (C).

Anal. Calcd for $C_7H_{14}ClNO$: C, 51.38; H, 8.62; N, 8.56; Cl, 21.66. Found: C, 51.29; H, 8.72; N, 8.45; Cl, 21.80.

5-Chloro-5-nitrosononane (4b)
Blue oil; R_f = 0.65 (petroleum ether).

^{1}H NMR (250.13 MHz, $CDCl_3$): δ = 0.86 (t, J = 6.9 Hz, 6 H, CH_3), 1.20–1.38 (m, 8 H, CH_2), 2.18–2.34 (m, 2 H, CH_2C), 2.53–2.67 (m, 2 H, CH_2C).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 13.7 (CH_3), 22.6 (CH_2CH_3), 25.3 ($CH_2CH_2CH_3$), 37.3 (CH_2C), 122.4 (C).

Anal. Calcd for $C_9H_{18}ClNO$: C, 56.39; H, 9.46; N, 7.31; Cl, 18.49. Found: C, 56.71; H, 9.63; N, 7.02; Cl, 18.21.

6-Chloro-6-nitrosoundecane (4c)[65]
Blue oil; R_f = 0.69 (petroleum ether).

^{1}H NMR (250.13 MHz, $CDCl_3$): δ = 0.85 (t, J = 6.9 Hz, 6 H, CH_3), 1.16–1.38 (m, 12 H, CH_2), 2.15–2.35 (m, 2 H, CH_2C), 2.50–2.66 (m, 2 H, CH_2C).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 13.7 (CH_3), 22.2, 22.8, 31.6 (CH_2), 37.5 (CH_2C), 122.1 (C).

2-Chloro-2-nitrosoadamantane (6)[67]
Blue crystals; mp 154–156 °C ($CHCl_3$) (Lit.[67] mp 161–163 °C); R_f = 0.57 (petroleum ether).

^{1}H NMR (250.13 MHz, $CDCl_3$): δ = 1.69–2.12 (m, 5 H, CH_2, CH), 2.22–2.51 (m, 9 H, CH_2, CH).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 26.87, 26.94, 34.3, 34.5, 34.7, 37.0, 37.5, 44.8 (CH_2, CH), 114.0 (C).

Anal. Calcd for $C_{10}H_{14}ClNO$: C, 60.15; H, 7.07; N, 7.01. Found: C, 60.25; H, 7.33; N, 6.88.

Chloronitro Compounds; General Procedure
Oxime (0.5 g, 2.09–5.05 mmol) was dissolved in CH_2Cl_2 (10 mL), a five-fold molar excess of aq 34% HCl (1.125–2.71 g, 10.45–25.25 mmol) was added, and the mixture was warmed to 38–40 °C. Then aq 37% H_2O_2 (four-fold molar excess) was added with stirring in 1 min, the mixture was stirred for 20 min, AcOH (HCO_2H) (10 mL) and a tenfold molar excess of aq 37% H_2O_2 (1.92–4.64 g, 20.9–50.5 mmol) were added, and the mixture was finally stirred at 25–30 °C for 2–12 h. If the conversion of the nitroso compound was incomplete, a five-fold molar excess of aq 37% H_2O_2 (0.96–2.32 g, 10.45–25.25 mmol) was added and the mixture was stirred until it turned colorless. Petroleum ether (50 mL) and H_2O (50 mL) were added, the lower aqueous layer was separated, and the upper layer was washed with H_2O (4 × 10 mL), dried ($MgSO_4$), and filtered. The filtrate was concentrated, and the target chloronitro compounds were isolated by flash chromatography using petroleum ether as the eluent.

5-Chloro-5-nitrononane (7b)[50]
Colorless oil; R_f = 0.52 (petroleum ether).

^{1}H NMR (250.13 MHz, $CDCl_3$): δ = 0.89 (t, J = 6.6 Hz, 6 H, CH_3), 1.15–1.65 (m, 8 H, CH_2), 2.09–2.43 (m, 4 H, CH_2C).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 13.7 (CH_3), 22.1 (CH_2CH_3), 26.2 ($CH_2CH_2CH_3$), 41.8 (CH_2C), 110.4 (C).

6-Chloro-6-nitroundecane (7c)
Colorless oil; R_f = 0.54 (petroleum ether).

^{1}H NMR (250.13 MHz, $CDCl_3$): δ = 0.89 (t, J = 6.6 Hz, 6 H, CH_3), 1.15–1.63 (m, 8 H, CH_2), 2.10–2.43 (m, 4 H, CH_2C).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 13.7 (CH_3), 22.2, 23.7, 31.0 (CH_2), 42.0 (CH_2C), 110.3 (C).

Anal. Calcd for $C_{11}H_{22}ClNO_2$: C, 56.04; H, 9.41; N, 5.94. Found: C, 56.28; H, 9.63; N, 5.81.

2-Chloro-2-nitroadamantane (8)[51]
White crystals; mp 190–191 °C ($CHCl_3$) (Lit.[51] mp 192–193 °C); R_f = 0.49 (petroleum ether).

^{1}H NMR (250.13 MHz, $CDCl_3$): δ = 1.70–2.82 (m, 14 H, CH_2, CH).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 25.5, 25.9, 34.1, 34.8, 37.0, 37.4 (CH_2, CH), 108.0 (C).

Anal. Calcd for $C_{10}H_{14}ClNO_2$: C, 55.69; H, 6.54; N, 6.49. Found: C, 55.28; H, 6.53; N, 6.18.

1-Chloro-1-nitrocyclopentane (9a)[49]
Colorless oil; R_f = 0.40 (petroleum ether).

^{1}H NMR (200.13 MHz, $CDCl_3$): δ = 1.75–2.05 (m, 4 H, CH_2), 2.25–2.43 (m, 2 H, CH_2C), 2.62–2.85 (m, 2 H, CH_2C).

^{13}C NMR (50.32 MHz, $CDCl_3$): δ = 23.1 (CH_2), 42.1 (CH_2C), 107.5 (C).

1-Chloro-1-nitrocyclohexane (9b)[52]
Colorless oil; R_f = 0.39 (petroleum ether).

^{1}H NMR (250.13 MHz, $CDCl_3$): δ = 1.49–1.85 (m, 6 H, CH_2), 2.20–2.49 (m, 4 H, CH_2C).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 22.9, 23.9 (CH_2), 38.2 (CH_2C), 103.7 (C).

1-Chloro-4-methyl-1-nitrocyclohexane (9c)
Colorless oil; mixture of isomers R_f = 0.45 (petroleum ether).

^{1}H NMR (250.13 MHz, $CDCl_3$): δ = 0.85–0.98 (m, 3 H, CH_3), 1.32–2.93 (m, 9 H, CH, CH_2).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 20.7, 21.2 (CH_3), 29.6, 30.7 (CH), 30.6, 31.4 (CH_2), 37.7, 37.9 (CH_2C), 101.4, 104.6 (C).

Anal. Calcd for $C_7H_{12}ClNO_2$: C, 47.33; H, 6.81; N, 7.89; Cl, 19.96. Found: C, 47.58; H, 6.55; N, 7.68; Cl, 19.62.

4-*tert*-Butyl-1-chloro-1-nitrocyclohexane (9d)[68]
Colorless oil; mixture of isomers; R_f = 0.47 (petroleum ether).

^{1}H NMR (250.13 MHz, $CDCl_3$): δ = 0.82 (0.88) (s, 9 H, t-C_4H_9), 1.05–2.28 (m, 7 H, CH, CH_2), 2.46–3.07 (m, 2 H, CH_2).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 23.5, 24.9, 26.9, 27.0, 31.5, 32.2 (C), 38.4, 38.8 (CH_2), 45.7, 46.3 (CH), 101.0, 104.8 (CCl).

1-Chloro-1-nitrocycloheptane (9e)[20]
Colorless oil; R_f = 0.46 (petroleum ether).

^{1}H NMR (250.13 MHz, $CDCl_3$): δ = 1.52–1.82 (m, 8 H, CH_2), 2.32–2.75 (m, 4 H, CH_2C).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 22.7, 28.2 (CH_2), 42.4 (CH_2C), 108.6 (C).

1-Chloro-1-nitrocyclooctane (9f)[68]
Colorless oil; R_f = 0.48 (petroleum ether).

^{1}H NMR (250.13 MHz, $CDCl_3$): δ = 1.51–1.88 (m, 10 H, CH_2), 2.20–2.81 (m, 4 H, CH_2C).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 22.9, 24.4, 27.4 (CH_2), 37.2 (CH_2C), 108.5 (C).

1-Chloro-1-nitrocyclododecane (9g)[21]
White crystals; mp 48.5–49.5 °C ($CHCl_3$) (Lit.[21] mp 49.5–50.5 °C); R_f = 0.52 (petroleum ether).

^{1}H NMR (250.13 MHz, $CDCl_3$): δ = 1.15–1.62 (m, 18 H, CH_2), 2.13–2.42 (m, 4 H, CH_2C).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 20.6, 22.0, 22.3, 25.5 (CH_2), 35.1 (CH_2C), 106.4 (C).

1-Chloro-1-nitrocyclopentadecane (9h)
Colorless oil; R_f = 0.57 (petroleum ether).

^{1}H NMR (250.13 MHz, $CDCl_3$): δ = 1.15–1.60 (m, 24 H, CH_2), 2.14–2.51 (m, 4 H, CH_2C).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 22.7, 26.5–26.8 (CH_2), 38.5 (CH_2C), 106.8 (C).

Anal. Calcd for $C_{15}H_{28}ClNO_2$: C, 62.16; H, 9.74; N, 4.83; Cl, 12.23. Found: C, 62.38; H, 9.43; N, 4.59; Cl, 12.01.

Acknowledgment

This work is supported by the Program for Support of Leading Scientific Schools of the Russian Federation (Grant NSh 5022.2006.3) and the Russian Science Support Foundation.

References

(1) Barhate, N. B.; Gajare, A. S.; Wakharkar, R. D.; Bedekar, A. V. *Tetrahedron* **1999**, *55*, 11127.
(2) Barhate, N. B.; Gajare, A. S.; Wakharkar, R. D.; Bedekar, A. V. *Tetrahedron Lett.* **1998**, *39*, 6349.
(3) Bora, U.; Bose, G.; Chaudhuri, M. K.; Dhar, S. S.; Gopinath, R.; Khan, A. T.; Patel, B. K. *Org. Lett.* **2000**, *2*, 247.
(4) Terent'ev, A. O.; Khodykin, S. V.; Troitskii, N. A.; Ogibin, Yu. N.; Nikishin, G. I. *Synthesis* **2004**, 2845.
(5) Terent'ev, A. O.; Khodykin, S. V.; Krylov, I. B.; Ogibin, Yu. N.; Nikishin, G. I. *Synthesis* **2006**, 1087.
(6) Arutyunyan, V. S.; Kochikyan, T. V.; Egiazaryan, N. S.; Avetisyan, A. A. *Russ. J. Org. Chem.* **1995**, *31*, 90; *Zh. Org. Khim*. **1995**, *31*, 100.
(7) Rudakova, N. I.; Anufrieva, O. V.; Smirnova, E. A. *J. Gen. Chem. USSR (Engl. Transl.)* **1992**, *62*, 1887: *Zh. Obshch. Khim*. **1992**, *62*, 2290.
(8) Rudakova, N. I.; Erykalov, Yu. G.; Zharikova, S. M.; Dmitrieva, E. V.; Mataradze, M. S. *Russ. J. Gen. Chem.* **1995**, *65*, 271; *Zh. Obshch. Khim*. **1995**, *65*, 315.
(9) Dakka, J.; Sasson, Y. *J. Chem. Soc., Chem. Commun.* **1987**, 1421.
(10) Bhatkhande, B. S.; Adhikari, M. V.; Samant, S. D. *Ultrason. Sonochem.* **2002**, *9*, 31.
(11) Vyas, P. V.; Bhatt, A. K.; Ramachandraiah, G.; Bedekar, A. V. *Tetrahedron Lett.* **2003**, *44*, 4085.
(12) Bezodis, P.; Hanson, J. R.; Petit, P. *J. Chem. Res., Synop.* **1996**, 334.
(13) Andrievskii, A. M.; Gorelik, M. V.; Avidon, S. V.; Al'tman, E. S. h. *Russ. J. Org. Chem.* **1993**, *29*, 1519; *Zh. Org. Khim*. **1993**, *29*, 1828.
(14) Hanson, J. R.; Opakunle, A.; Petit, P. *J. Chem. Res., Synop.* **1995**, 457.
(15) Tillu, V. H.; Shinde, P. D.; Bedekar, A. V.; Wakharkar, R. D. *Synth. Commun.* **2003**, *33*, 1399.
(16) (a) Mukhopadhyay, S.; Ananthakrishnan, S.; Chandalia, S. B. *Org. Process Res. Dev.* **1999**, *3*, 10. (b) Mukhopadhyay, S.; Ananthakrishnan, S.; Chandalia, S. B. *Org. Process Res. Dev.* **1999**, *3*, 196. (c) Mukhopadhyay, S.; Ananthakrishnan, S.; Chandalia, S. B. *Org. Process Res. Dev.* **1999**, *3*, 451.
(17) Espenson, J. H.; Zhu, Z.; Zauche, T. H. *J. Org. Chem.* **1999**, *64*, 1191.
(18) Sharma, V. B.; Jain, S. L.; Sain, B. *Synlett* **2005**, 173.
(19) Taylor, R. *Electrophilic Aromatic Substitution*; Wiley: New York, **1990**.
(20) Corey, E. J.; Estreicher, H. *Tetrahedron Lett.* **1980**, *21*, 1117.
(21) Sakai, I.; Kawabe, N.; Ohno, M. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 3381.
(22) Tordeux, M.; Boumizane, K.; Wakselman, C. *J. Fluorine Chem.* **1995**, *70*, 207.
(23) Archibald, T. G.; Baum, K. *J. Org. Chem.* **1988**, *53*, 4645.
(24) Arbuzov, Yu. A.; Markowskaja, A. *Bull. Acad. Sci. USSR Div. Chem. Sci. (Engl. Transl.)* **1952**, 355; *Izv. Akad. Nauk SSSR Ser. Khim.* **1952**, 363.
(25) Belleau, B.; Au-Young, Y.-K. *J. Am. Chem. Soc.* **1963**, *85*, 64.
(26) Arbuzov, Yu. A.; Onishchenko, A. A. *Dokl. Chem. (Engl. Transl.)* **1962**, *146*, 875; *Dokl. Akad. Nauk SSSR*, **1962**, *146*, 1075.
(27) Iida, H.; Watanabe, Y.; Kibayashi, C. *J. Org. Chem.* **1985**, *50*, 1818.
(28) Nelsen, S. F.; Thompson-Colon, J. A.; Kirste, B.; Rosenhouse, A.; Kaftory, M. *J. Am. Chem. Soc.* **1987**, *109*, 7128.
(29) Kresze, G.; Kysela, E.; Dittel, W. *Liebigs Ann. Chem.* **1981**, 210.
(30) Werbitzky, O.; Klier, K.; Felber, H. *Liebigs Ann. Chem.* **1990**, 267.
(31) Kresze, G.; Dittel, W. *Liebigs Ann. Chem.* **1981**, 610.
(32) Schuerrle, K.; Beier, B.; Piepersberg, W. *J. Chem. Soc., Perkin Trans. 1* **1991**, 2407.
(33) Iida, H.; Watanabe, Y.; Kibayashi, C. *Tetrahedron Lett.* **1984**, *44*, 5091.
(34) Shi, G.-Q.; Schlosser, M. *Tetrahedron* **1993**, *49*, 1445.
(35) Ranganathan, D.; Ranganathan, S.; Rao, C. B.; Raman, K. *Tetrahedron* **1981**, *37*, 629.
(36) Defoin, A.; Joubert, M.; Heuchel, J.-M.; Strehler, C.; Streith, J. *Synthesis* **2000**, 1719.
(37) Filip, S. V.; Sewald, N. *Synthesis* **2005**, 3565.
(38) Morris, A. D.; Frinault, T.; Benhida, R.; Gharbaoui, T.; Lechevallier, A.; Beugelmans, R. *Bull. Soc. Chim. Fr.* **1995**, *132*, 178.
(39) Archibald, T. G.; Garver, L. G.; Baum, K.; Cohen, M. C. *J. Org. Chem.* **1989**, *54*, 2869.
(40) Ono, N.; Tamura, R.; Hayami, J.-i.; Kaji, A. *Chem. Lett.* **1977**, 189.
(41) Russell, G. A.; Mudryk, B.; Jawdosiuk, M. *Synthesis* **1981**, 62.

(42) Ono, N.; Tamura, R.; Eto, H.; Hamamoto, I.; Nakatsuka, T. *J. Org. Chem.* **1983**, *48*, 3678.
(43) Russell, G. A.; Hershberger, J. *J. Chem. Soc., Chem. Commun.* **1980**, 216.
(44) Müller, E.; Fries, D.; Metzger, H. *Chem. Ber.* **1955**, *88*, 1891.
(45) Mackor, A.; de Boer, Th. J. *Recl. Trav. Chim. Pays-Bas* **1970**, *89*, 151.
(46) Wichterle, O.; Hudlicky, M. *Collect. Czech. Chem. Commun.* **1947**, *12*, 661.
(47) Hammick, D. L.; Lister, M. W. *J. Chem. Soc.* **1937**, 489.
(48) Kumar, V.; Kaushik, M. P. *Tetrahedron Lett.* **2005**, *46*, 8121.
(49) Barnes, M. W.; Patterson, J. M. *J. Org. Chem.* **1976**, *41*, 733.
(50) Ceccherelli, P.; Curini, M.; Epifano, F.; Marcotullio, M. C.; Rosati, O. *Tetrahedron Lett.* **1998**, *39*, 4385.
(51) Walters, T. R.; Zajac, W. W. Jr.; Woods, J. M. *J. Org. Chem.* **1991**, *56*, 316.
(52) Zaks, A.; Yabannavar, A. V.; Dodds, D. R.; Evans, C. A.; Das, P. R.; Malchow, R. *J. Org. Chem.* **1996**, *61*, 8692.
(53) Moiseev, I. K.; Mratkhuzina, T. A.; Makarova, N. V. *Russ. J. Gen. Chem.* **1999**, *69*, 1777; *Zh. Obshch. Khim.* **1999**, *69*, 1855.
(54) Makosza, M.; Kwast, A.; Kwast, E.; Jonczyk, A. *J. Org. Chem.* **1985**, *50*, 3722.
(55) Amrollah-Madjdabadi, A.; Beugelmans, R.; Lechevallier, A. *Synthesis* **1986**, 826.
(56) Barber, G. N.; Olofson, R. A. *J. Org. Chem.* **1978**, *43*, 3015.
(57) Johnston, T. P.; McCaleb, G. S.; Opliger, P. S.; Laster, W. R.; Montgomery, J. A. *J. Med. Chem.* **1971**, *14*, 600.
(58) Simunic-Meznaric, V.; Mihalic, Z.; Vancik, H. *J. Chem. Soc., Perkin Trans. 2* **2002**, 2154.
(59) Ruzicka, L.; Kobelt, M.; Häfliger, O.; Prelog, V. *Helv. Chim. Acta* **1949**, *32*, 544.
(60) Sacharkin, L. I.; Shigarewa, G. G. *Bull. Acad. Sci. USSR Div. Chem. Sci. (Engl. Transl.)* **1962**, 168; *Izv. Akad. Nauk SSSR Ser. Khim.* **1962**, 183.
(61) Adamopoulos, S.; Boulton, A. J.; Tadayoni, R.; Webb, G. A. *J. Chem. Soc., Perkin Trans. 1* **1987**, 2073.
(62) Wilcox, M.; Taylor, J. B. (Ciba-Geigy A.-G.) Ger. Offen. 2338010, *Chem. Abstr.* **1974**, *80*, 132803.
(63) von Braun, J.; Kröper, H. *Chem. Ber.* **1929**, *62*, 2883.
(64) Battiste, D. R.; Traynham, J. G. *J. Org. Chem.* **1975**, *40*, 1239.
(65) Kosinski, M. *Soc. Sci. Lodz. Acta Chim.* **1964**, *9*, 93.
(66) Dieckmann, H.; Luettke, W. *Chem. Ber.* **1972**, *105*, 1899.
(67) Funabashi, M.; Tanaka, A.; Anselme, J. P. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 2958.
(68) Curini, M.; Epifano, F.; Marcotullio, M. C.; Rosati, O.; Rossi, M. *Tetrahedron* **1999**, *55*, 6211.